(12)

REPORT DRXTH-TE-CR-82179

SURFACE SAMPLING TECHNIQUES

Bruce E. Goodwin
James R. Aronson
Robert P. O'Neil
Margaret A. Randel
Emmett M. Smith

ARTHUR D. LITTLE, INC.
CAMBRIDGE, MA 02140

SEPTEMBER, 1982

FINAL REPORT
Volume I
Distribution Unlimited
Cleared for Public Release

prepared for

U.S. Army Toxic and Hazardous Materials Agency,
Aberdeen Proving Ground, Maryland 21010

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Qualitative and quantitative sampling and analysis methods for the detection and determination of explosives/nonexplosive residues on building materials surfaces are described. Quantitative certification testing data for a solvent extraction - HPLC method are included.

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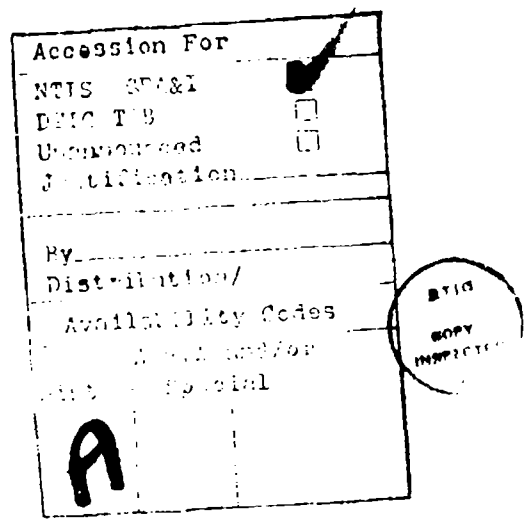
SUMMARY

Under Contract No. DAAK11-81-C-0014 to the U. S. Army Toxic and Hazardous Materials Agency, Arthur D. Little, Inc. has developed sampling protocols for the determination of explosives/explosive residues on building materials surfaces. The Army's need for this sampling and analysis capability has arisen in connection with the release of surplus government property (e.g., former ammunition plants) and the specified requirement that as part of these release programs, a determination be made as to whether the property can be released for unrestricted use. In the case of buildings known or suspected to have been contaminated with explosives, the Army is seeking for this purpose sampling and analytical procedures which would permit: (1) rapid qualitative determination with 90% confidence of the presence/absence of the compounds of interest down to a level of 5 μg/10 cm^2 in a given building, and (2) if any of these compounds is detected, precise, accurate quantitative determination of the amount of contamination down to the same 5 μg/10 cm^2 level.

This study resulted in the development of several methods for the sampling and analysis of explosives/explosive residues on building materials surfaces. A method for qualitative determination based on detection of charge-transfer complexes formed between the explosive/explosive residue and a visualization reagent applied to the surface has been evaluated in the field at two Army Ammunition Plants. A method for quantitative determination based on solvent extraction of samples collected in the field followed by high pressure liquid chromatographic analysis has been evaluated on samples prepared in the laboratory, and found to give promising results. The theoretical and practical feasibility of another method for qualitative determination based on UV irradiation of a suspected contaminated surface with subsequent detection of any explosives/explosive residues present has been demonstrated. This approach may provide the means for "scanning" an area to determine whether explosives are present on a real-time basis. Further development of this approach is recommended.



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I. INTRODUCTION

Under Contract No. DAAK11-81-C-0014 to the U.S. Army Toxic and Hazardous Materials Agency, Arthur D. Little, Inc. has developed sampling protocols for the determination of explosives/explosive residues on building materials surfaces. The Army's need for this sampling and analysis capability has arisen in connection with the release of surplus government property (e.g., former ammunition plants) and the specified requirement that as part of these release programs, a determination be made as to whether the property can be released for unrestricted use. In the case of buildings known or suspected to have been contaminated with explosives, the Army is seeking for this purpose sampling and analytical procedures which would permit: (1) rapid qualitative determination with 90% confidence of the presence/absence of the compounds of interest down to a level of 5 $\mu g/10\ cm^2$ in a given building, and (2) if any of these compounds is detected, precise, accurate quantitative determination of the amount of contamination down to the same 5 $\mu g/10\ cm^2$ level.

The specific compounds and surface types of interest were the following:

Compounds

1. 2,4,6-trinitrotoluene (TNT)
2. 2,4- and 2,6-dinitrotoluene
3. Cyclotrimethylenetrinitramine (RDX)
4. Pentaerythrite tetranitrate (PENT)
5. Nitroglycerine
6. 2,4,6-trinitrophynylmethylnitramine (Tetryl)
7. Diphenylamine
8. 1,3,5-trinitrobenzene
9. 2,4-dinitrophenol
10. Cd
11. Pb
12. Hg
13. Cr^{+3}
14. Cr^{+6}

Surface Types

1. Concrete--unpainted
2. Brick--glazed and unglazed
3. Transite
4. Wood
5. Metal
6. Conducting non-sparking floor

The approach that was taken to the development of these sampling protocols involved the following steps:

A. Literature Search
B. Sampling Protocol Selection
C. Analytical Method Selection/Development
D. Certification Testing
E. Development of a Spike and Recovery Test Plan
F. Spike and Recovery Testing
G. Interference Testing

The Literature Search provided an overview of existing sampling and analysis methods. The results of the literature search suggested that most existing methods would not satisfy the Army's requirements as stated above. Thus, in the Sampling Protocol Selection step, several approaches based on technology developed for applications other than explosives analysis were proposed for further development. Those approaches involved methods intended specifically for qualitative analysis, and a method intended specifically for quantitative analysis of explosives/explosive residues on surfaces.

Development of the quantitative analysis method proceeded with an Analytical Method Selection/Development step, in which advantage was taken of the fact that several methods for the determination of explosives were present in the USATHAMA data base. These methods were modified as necessary to permit their application to the present study, and the precision and accuracy for each of the resulting methods were assessed in preliminary Certification Testing (semiquantitative).

Subsequent to approval by the Technical Project Officer of a Spike and Recovery Test Plan, methods for each analyte on each surface type were evaluated by Spike and Recovery Testing. Finally, methods were subjected to Quantitative Certification Testing according to the requirements in the 1980 USATHAMA QA Plan. Since most of the analytes are determined in a single extract, the need for Interference Testing in the laboratory was largely eliminated, interferences from other sources which may be present in samples collected in the field were not addressed in this study.

This study resulted in the development of several methods for the sampling and analysis of explosives/explosive residues on building materials surfaces. A method for qualitative determination based on detection of charge-transfer complexes formed between the explosive/explosive residue and a visualization reagent applied to the surface has been evaluated in the field at two army ammunition plants. A method for quantitative determination based on solvent extraction of samples collected in the field followed by high pressure liquid chromatographic analysis has been evaluated on samples prepared in the laboratory, and found to give promising results. The theoretical and practical feasibility of another method for qualitative determination based on UV irradiation of a suspected contaminated surface with subsequent detection of any explosives/explosive residues present has been demonstrated. This approach may provide the means for "scanning" an area to determine whether explosives are present on a real-time basis. Further development of this approach is recommended. No methods for inorganic species which would represent substantive improvement over existing qualitative and quantitative methods were identified.

Detailed discussions of these areas of investigation are presented in the remaining sections of this report.

II. SAMPLING AND ANALYSIS METHODS SELECTION

A. INTRODUCTION:

The available literature on the sampling and chemical analysis of explosives/explosive residues was reviewed to provide an overview of existing sampling and analysis methods prior to selection of specific approaches for further development. The findings of that review are described below.

B. LITERATURE SEARCH:

Work was initiated by conducting a literature search to identify existing sampling and analytical methods for explosives which might be applicable to the particular problem of detecting and determining those same materials on building materials surfaces.

1. Approach.

There were basically two problems that had to be resolved in order to develop appropriate strategies for the computerized literature searchings: (1) if the search strategy involved the fifteen defined analytes in combination with the defined surfaces, as well as with general terms such as surface sampling, recovery, sample selection, detection, etc., the search results were nil; and (2) if the search strategy involved the use of such general terms as explosives, ammunition, and dynamite, as well as the Chemical Abstracts Section 50 (Explosives and Propellants), combined with terms such as analysis, sampling, recovery, identification, determination, etc., the search results were not applicable to this study.

The techniques used in the forensic sciences appeared appropriate for the recovery and analysis of the analytes under consideration; therefore, the search strategy that yielded the most relevant citations involved the combination of the Chemical Abstracts Forensic Analysis Subsection, the Registry Numbers of the 15 analytes, and the terms explosives, dynamite, and ammunition.

2. Sources and Coverage.

The search for applicable techniques for surface sampling for explosives/explosive by-products has been performed on:

Source	Coverage	Number of Citations
Chemical Abstracts	1967 - present	164

The 164 citations were reviewed for duplication and extraneous material and were reduced to an output of 45 citations. This output was reviewed and the 45 citations for document retrieval.

In addition to the computerized search of Chemical Abstracts, a manual review of a National Technical Information Service (NTIS) bibliography with abstracts, entitled Pollution Caused by Ammunition Manufacturing, was undertaken. Of 237 abstracts, 9 appeared appropriate for review and were ordered.

The following computerized data bases were also searched:

APTIC
ENVIROLINE
POLLUTION ABSTRACTS
SCISEARCH
NTIS
CRIS (Current Research Information Systems)
SSIE Current Research
CONFERENCE PAPERS INDEX

3. Results.

The results of the literature search are summarized in Tables II-1 through II-4. Table II-1 is a bibliography of useful citations including (1) the authors' abstracts or brief summaries taken directly from the article, describing the purpose and results of the work described in the article, and (2) comments describing potential applications of the work described in each article to this study; Table II-2 lists the analytes of interest in this study for which sampling and/or analysis procedures are described in each article with detection limits, when included in the article, listed under the respective headings in the table; Table II-3 lists the analytical methods used or recommended in each article for determination of analytes of interest in this study; Table II-4 lists (1) the sampling procedures used or recommended in each article for analytes of interest in this study, (2) any additional sample preparation procedures required subsequent to sampling and prior to analysis, and (3) any interferences described in the article with the sampling and/or analytical procedures.

TABLE II-1. BIBLIOGRAPHY OF USEFUL CITATIONS

ARTICLE NUMBER	REFERENCE	AUTHOR ABSTRACT	COMMENTS
1	Ames, S.A.M.; Yallop, H.J. A Test for Cyclotrimethylene-trinitramine. Analyst (9):578; 1969.	The familiar spot test for the identification of cyclotrimethylenetrinitramine, RDX, is based on the production of the red colour formed by this compound in the presence of thymus and nitrogen-free sulphuric acid. An objection to this test is, however, that a red colour is produced by other compounds, in particular sugars and aldehydes; a deep pink colour may be produced unless the sulphuric acid is of the quality marketed as "nitrogen free." A method of surmounting this difficulty has been found.	Specific colorimetric test for RDX; would require separation of sample from surface; 100°C heat source required; which may be difficult in field applications.
2	Ames, S.A.M.; Yallop, H.J. The Detection of Dinitro and Trinitro Aromatic Bodies in Industrial Blasting Explosives. Analyst 91(5):336-337; 1966.	The detection and identification of nitro-bodies is a common requirement in the explosives laboratory. The addition of a 5 to 10-mg specimen of one drop of acetone-alcohol, and one drop of tetramethylammonium hydroxide provides a blue color with dinitrotoluene and a dark red with trinitrotoluene. The test has been applied to a wide range of obsolete and current industrial blasting explosives and it has been found that none of the other components present interfere with the reaction.	May be useful as spot test for 2,4-DNT and 2,4,6-TNT directly on surface; interferences from explosive types other than nitro-compounds not discussed.
3	Ames, S.A.M.; Yallop, H.J. The Identification of Industrial Blasting Explosives of the Gelignite Type. J. Forensic Sci. Soc. (4):185-188; 1966.	Samples of explosive found at a scene have often deteriorated and tend to be small, unrepresentative and contaminated with material from the surroundings. This paper describes a new approach to the identification of such exhibits. The method consists in determining the presence or absence of as many as possible of the commonly used ingredients by simple chemical tests done on a spot plate. The results are then compared with the manufacturer's data and in most cases, it is found that there is only one explosive with the combination of ingredients identified. A full identification of a sample unknown explosive can often be done in about 10 minutes.	May be useful as spot test for 2,4-DNT, 2,6-DNT, 2,4,6-TNT, NC, RDX; RINKS used for detection of 2,4- and 2,6-DNT and PDA are identical to those in Refs. 1 and 2, except test for RDX does not require heating; interferences from explosives of types other than those listed not discussed.
4	Andrasko, J.; Maehly, A.C. Detection of Gunshot Residues by Scanning Electron Microscopy. J. Forensic Sci. 22(2):279-287; 1977.	Previously reported methods make use of only the chemical composition of the entire sample taken from the firing hand for the presence of gunshot residues. In the present study, scanning electron microscopy (SEM) makes it possible to establish the shape and appearance of the individual particle. Only those objects which look like gunshot residues are analyzed. The combination of these two criteria would be expected to increase.	Limited to elemental analysis; probably not useful in this study except as screening or confirmatory technique.

TABLE II-1. BIBLIOGRAPHY OF USEFUL CITATIONS (CONTINUED)

ARTICLE NUMBER	REFERENCE	AUTHOR ABSTRACT	COMMENTS
5	Smith, A.; Crumm, S. Analytical and Characterization of Military-Grade Trinitrotoluene by Gas Chromatography. J. Forensic Sci. 24(4):870-874; 1979	We wish to report improved GC procedures for the separation of isomers and other impurities present in military-grade TNT. These procedures, when combined with standardized extraction techniques for concentration of the impurities, permit detection and semiquantitative measurement of up to 2% impurities in typical samples. This combined extraction-GC procedure determines impurities present in commercial samples of TNT at levels as low as 0.001%.	GC conditions given for determination of DNT and trinitrobenzene down to 0.001% in TNT; FID detector used; analysis performed on hexane extract of TNT sample.
6	Beveridge, A.D.; Preston, S.P.; Audette, R.J.; Lamberton, A.J.; Chaddick, R.C. Systematic Analysis of Explosive Residues. J. Forensic Sci. 20(3):431-454; 1975.	This study presents a scheme for systematic analysis of explosive residues isolated by physical removal or solvent extraction. The techniques are a combination of infrared spectroscopy, TLC, X-ray diffraction, emission spectrography, microscopy, and chemical spot tests.	TLC and IRD used as prime identification techniques for high explosives with other materials used for confirmation. Analyses performed on ether and acetone extracts from steel, wood, and ceiling tile. Colorimetric visualization used in TLC.
7	Canfield, D.V.; DeForest, P.R. The Use of the Gandolfi Camera as a Screening and Confirmation Tool in the Analysis of Explosive Residues	An ideal technique would have to be both sensitive and definitive and, in addition, should be able to deal with the contamination problem encountered with actual explosive residue samples. This ideal is closely approached for crystalline residues by the Gandolfi camera, which is capable of producing a detailed X-ray diffraction pattern for a single microscopic crystal. Contamination difficulties can be eliminated if the requisite intact microscopic crystals can be found in the residue. Locating, mechanically removing, and identifying these crystals eliminates the need for a preliminary solvent extraction with its attendant contamination problem.	Probably not useful in this study due to unusual instrumentation requirement.
8	Chandler, C.D.; Kohlbeck, J.A.; Bolleter, W.T. Continuous TNT Process Studies. III. Thin-Layer Chromatographic Analysis of Oxidation Products from Nitration. J. Chromatogr. 64:123-126; 1972.	Thin-layer chromatograph separations are shown of all major oxidation products from various steps of the continuous TNT nitration process and of nitration compounds resulting from impurities in the toluene used for nitration.	TLC conditions for nitro-compounds. Visualization with UV light and subsequent colorimetric development.
9	Chasan, D.E.; Horwitz, G. Qualitative Analysis of Primers, Tracers, Igniters, Incendiaries, Boosters, and Delay Compositions on a Microscale by Use of Infrared Spectroscopy. Microchem. J. 17: 51-60;1972	This laboratory undertook an investigation on the application of infrared spectroscopy to the detection of the organic compounds and inorganic compounds present in primers, tracers, igniters, incendiaries, boosters, and delay compositions.	Probably not useful in this study except as screening or confirmatory technique. Relatively large sample size (i.e., 1-2 mg) requirements.

TABLE II-1. BIBLIOGRAPHY OF USEFUL CITATIONS (CONTINUED)

ARTICLE NUMBER	REFERENCE	AUTHOR ABSTRACT	COMMENTS
10	Chrostowski, J.R.; Holmes, R.N.; Rehn, B.W. The Collection and Determination of Ethylene Glycol Dinitrate, Nitroglycerine, and Trinitrotoluene Explosive Vapors. J. Forensic Sci. 21(3):611-615; 1976.	This paper describes the use of a short column containing porous polymer beads to collect explosive vapors of ethylene glycol dinitrate (EGDN), nitroglycerine (NG), and trinitrotoluene (TNT), with subsequent analysis by TCL.	Collection of analytic vapors may provide a means of eliminating interferences encountered in solvent extraction sampling methods. Quantitative capabilities of method for determination of analytes at extended time after deposition uncertain.
11	Cowan, M.E.; Purdon, P.L. A Study of the "Paraffin Test." J. Forensic Sci. 12(1):19-36; 1967.	It is [the author's] opinion that a frank discussion and demonstration of the fallability of the so-called "Paraffin Test" would be appropriate ....Attention has been directed to evaluating reagents, improving techniques of casting and application of reagent, as well as devising a satisfactory manner of recording the reactions.	Non-specific test for nitrate. Probably not useful in this study due to large numbers of potential interferences.
12	Doali, J.O.; Juhasz, A.A. Application of High Speed Liquid Chromatography to the Qualitative Analysis of Compounds of Propellant and Explosives Interest. J. Chromatogr. Sci. 12(1):51-56; 1974.	The analysis of energetic compounds is often complicated by their low volatility and low thermal stability. A potentially useful technique for such analyses is high speed liquid chromatography since it does not require sample heating or vaporization. The use of the method is illustrated using synthetic mixtures of components found in explosive formulations. Separations involving nitrate esters, nitroaromatic compounds and nitramines are discussed. The use of the technique for the analysis of single and double base propellants is also presented.	Conditions given for separation of synthetic mixtures containing various analytes of interest on Corasil II column, UV detector.
13	Elie-Calmet, J.; Forestier, H. Characterization of Explosives' Traces After an Explosion. Int. Crim. Police Rev. Series 325:38-47; 1979.	In complicated cases of explosive mixtures, degraded explosives, explosives containing copolymerised plasticisers, or with impurities present, the chromatographic separation detailed in [a previous article by these authors] may be inconclusive. Furthermore, specific chromatographic separation may be required to detect the explosive constituents. [In this article] the authors describe how to test for various nitro esters.	The conditions for separation of various explosives. Visualization method not specified.
14	Fisco, N. A Portable Explosives Identification Kit for Field Use. J. Forensic Sci. 20:141-147; 1975.	In this work the approach was to develop a field kit that incorporated a nondestructive uniform analytical technique with emphasis on protability, ease of operation, and low cost. The report details the modification of a commercially available portable kit for the achievement of these objectives.	TLC conditions for separation of various explosives. Uses commercially available portable TLC kit and battery-powered UV lamp for vizualization of resolved constituents. May be nday adapted for this study if conditions for resolution and visualization of other analytes of interest can be demonstrated.

TABLE II-1. BIBLIOGRAPHY OF USEFUL CITATIONS (CONTINUED)

ARTICLE NUMBER	REFERENCE	AUTHOR ABSTRACT	COMMENTS
15	Gagliano Candela, R.; Colonna, M.; Strada, L. Identification of the Explosion Residues of Shots from Firearms by Anodic Stripping Polarography. Zacchia 12(1):44-52; 1976. CAS No. 85:154648j.	Pb and Sb, present in common commercial firearm detonators, were determined by anodic stripping polarography on the hands of persons having fired revolvers. The hands were cleaned with filter paper moistened with HNO_3 and the ashed paper was was analyzed in a commercial apparatus.	Useful for metals only.
16	Gislason, J.; Pate, B.D. Studies of Gunshot Residue. J. Radioanalytical Chem. 15:103-113; 1973.	The deposits resulting from the discharge of 0.22 calibre ammunition have been studied by neutron activation analysis and autoradiography.	Useful for elemental analysis only. Probably not useful in this study due to unusual instrumentation requirement.
17	Goleb, J.A.; Midkiff, C.R. Firearms Discharge Residue Sample Collection Techniques. J. Forensic Sci. 20: 701-707; 1975.	Of the various collection systems currently in use, only cotton swabs and film-lifting procedures appeared to combine ease of use in the field with suitability for rapid laboratory examination by FAAS. However, one additional material, transparent adhesive tape, also appeared suitable for routine use. This material is readily available, inexpensive, convenient to use, and amenable to reproducible sample collection.	Sample collection methods used for determination of metals (Ba and Sb), and may not be applicable (except for cotton swab technique) for determination of organic compounds.
18	Hoffman, C.M.; Byall, E.C. Identification of Explosive Residues in Bomb Scene Investigations. J. Forensic Sci. 19:54-6); 1974.	Bioluminescence may be useful for detecting explosive traces. In this technique, special cultures are sensitized to vapors from a specific explosive and respond to the presence of this explosive by the emission of light. While there are some difficulties with this approach, such as the lengthy activation time of the culture when a new detector cell must be prepared, the bioluminescence units are compact, portable, relatively inexpensive, and do not require extensive operator training. Particles of the explosive used in a bomb can usually be recovered from properly collected debris taken at the scene if the debris is meticulously examined microscopically. The explosive can then be identified by rather simple chemical and instrumental procedures. As a last resort, solvent extraction of the debris may be performed, but this is not recommended since it usually lacks the specificity and sensitivity necessary to detect the traces of explosive present in a large volume of debris. In addition, the debris may contain substances that would interfere with subsequent tests of the extract. Cotton swabs soaked in acetone are effective in removing traces of various explosives from the hands of a subject who has recently handled them. Explosive residues on the swabs can be identified in the laboratory by TLC Procedures. Instruments such as the ETA have value in rapidly scanning debris, cotton hand swabs, clothing, and air samples for the presence of explosives. The explosive present is then confirmed by chemical methods.	Summary article including recommendations of specific sampling and analysis procedures described in other references. Bioluminescence technique not discussed in detail, but may be worth further investigation.

TABLE II-1. BIBLIOGRAPHY OF USEFUL CITATIONS (CONTINUED)

ARTICLE NUMBER	REFERENCE	AUTHOR ABSTRACT	COMMENTS
19	Hoffsommer, J. Quantitative Analysis of Nitro Compounds in the Micro- to Picogram Range by a Combination of Thin-Layer and Vapor Phase Chromatography With the Nickel-6_3 Electron Capture Detector. J. Chromatog. 51: 243-251; 1970.	A method has been developed for the quantitative analysis of nitro compounds in the micro- to picogram range by a combination of thin-layer and vapor phase chromatography employing the nickel-6_3 electron capture detector. The relative electron absorptivities of ten nitro compounds have been measured with 1,3,5-trinitrobenzene as a standard. Experimental variables affecting the nickel-6_3 electron capture detector are presented.	Conditions to separation of nitro compounds by TLC, visualization by UV with set limits >0.4 pg/spot; spots removed fr m TLC plate by scraping and then extracted; nitro compounds in extracts quantitated by GC with Ni-6_3 detector with recoveries >95% for compounds tested; disadvantage is that Ni-6_3 detector is easily contaminated or overloaded.
20	Jenkins, R.; Tallop, H.J. The Identification of Explosives in Trace Quantities on Objects Near an Explosion. Explosivstoffe Nr 6:139-141; 1970.	A [TLC] technique is described whereby traces of explosive adhering to surrounding objects after an explosion can be detected and identified. The method has also been applied to the identification of traces on the skin and clothing of persons suspected to have been in contact with explosives.	The conditions given for separation of various explosives: colorimetric visualization.
21	Jones, P.T.; Hamblin, E.S. A Photoluminescence Technique for Detection of Gunshot Residue. J. Forensic Sci. 20(2):231-242; 1975.	In our study we concentrated on the development of a molecular photoluminescence technique to detect metallic elements in gunshot residue. As discussed subsequently, the use of this technique is attractive because of the ease of analysis and its sensitivity and low cost. In this preliminary study we were concerned with the detection of Pb, Sb, and Ba.	Useful for metals only.
22	Kaplan, M.A.; Zitrin, S. Identification of Post-Explosion Residues. J.A.O.A.C. 60(3):619-624.	A scheme for the identification of explosive residues from post-explosion scenes is described. The first step consists of organic and inorganic extractions rather than microscopic examination. The methods of identification which follow include thin layer and gas-liquid chromatography, infrared and ultraviolet spectroscopy, and chemical tests. The system, which has been used routinely by the Israel Police for 5 years, deals efficiently with standard military explosives as well as with home-made, improvised mixtures.	Conditions given for various methods used for qualitative identification.
23	Kelsall, J.P.; Burton, R. Variability in the Chemical Contamination Effects of Gun Shot. J. Radioanal. Chem. 31:455-459; 1976.	This is a contribution to a larger study aimed at development of a technique to determine the origins of waterfowl from their feather chemistry, using automated X-ray fluorescence spectrometry. Since feather samples commonly come from shot birds, an effort was made to measure the contamination effects of shot using cotton cloth to simulate feathers. At pointblank ranges contamination can include the elements Ba, Sb, Pb, Cu, S and likely others depending on the exact composition of both gun powder and shot.	Useful for metals only.
24	Kempe, C.R.; Tannert, W.K. Detection of Dynamite Residues on the Hands of Bombing Suspects. J. Forensic Sci. 12(2):323-324; 1972.	Studies were undertaken using TLC for the identification of nitrate esters such as nitroglycerine, ethylene glycol dinitrate, and pentaerythritol tetranitrate (PETN). An attempt was made to show the reliability of TLC as a means of identification of these nitrated esters when removed from the hands.	TLC conditions given for separation of various explosives; colorimetric visualization.

TABLE II-1. BIBLIOGRAPHY OF USEFUL CITATIONS (CONTINUED)

ARTICLE NUMBER	REFERENCE	AUTHOR ABSTRACT	COMMENTS
25	Konanur, N.K.; vanLoon, G.W. Determination of Lead and Antimony in Firearm Discharge Residues by Anodic Stripping Voltammetry. Talenta 24:184-187; 1977.	In this study conditions for the determination of lead and antimony in gunshot residues by anodic stripping voltammetry using a mercury-coated graphite electrode are established. A sample is collected by washing the hand in 1M hydrochloric acid. Lead is determined in a portion of this sample, with 1M hydrochloric acid as electrolyte. Antimony is determined in a second portion, with 4M hydrochloric acid as electrolyte. Prior separation or preconcentration steps are not required for either analysis. The procedure has been applied to samples obtained from five "normal" hands and five hands after they have fired a weapon.	Useful for metals only. Sample obtained by washing hand in 1M HCl.
26	Krishnan, S.S. Detection of Gunshot Residue on the Hands by Neutron Activation and Atomic Absorption Analysis. J. Forensic Sci. 19(4): 789-797; 1974.	Because the amounts of the elements analyzed are at microgram levels, specially designed procedures and training are required to be able to collect the samples without contamination. The existing techniques, such as paraffin lift and cotton swabbing, are found to be unsatisfactory in this respect. By taking repeated samples from hands by these procedures, it was found that three or four collections are required for complete removal of the trace elements. Thus, a single collection by these methods is not quantitative, and therefore, any subsequent calculation would be in error. Neutron activation analysis is not effective in detecting lead, which is one of the important constituents of leakage residues. Hence, a method such as atomic absorption spectrometry (AAS) must be used in addition to NAA for this analysis.	Useful for metals only. Sample obtained by washing hand in 1M HNO_3.
27	Liu, J.N.; Lin, W-F.; Nicol, J.D. The Application of Anodic Stripping Voltammetry to Forensic Science. II. Anodic Stripping Voltammetric Analysis of Gunshot Residues. Forensic Sci. Intl. 16:53-62; 1980.	Non-destructive analysis of gunshot residues on hands was studied by anodic stripping voltammetry using a low-cost home-constructed polarograph. The washing solution was 0.5M HCl. Antimony was first analyzed in 4M HCl solution; and zinc, lead and copper were then simultaneously analyzed in 0.2 M acetate buffer (pH 5.9 ±0.1).	Useful for metals only. Sample obtained by washing hand in 1) detergent, 2) 0.5 M HCl.
28	Liu, J.N.; Taylor, L. The Application of Anodic Stripping Voltammetry to Forensic Science. Forensic Sci. Intl. 16:43-52; 1980.	An anodic stripping procedure was developed for the simultaneous determination of a zinc, cadmium, lead, antimony and copper mixture, and used for testing the instrument. Effects of pre-electrolysis time, concentration changes, presence of other species and overlapping were also studied.	Useful f metals only.

TABLE II-1. BIBLIOGRAPHY OF USEFUL CITATIONS (CONTINUED)

ARTICLE NUMBER	REFERENCE	AUTHOR ABSTRACT	COMMENTS
29	Lloyd, J.B. Detection of Microgram Amounts of Nitroglycerin and Related Compounds. J. Forensic Sci. Soc. 7: 198; 1967.	Nitrate esters, on hydrolysis, partly disproportionate to carbonyl compounds and nitrous acid. This has provided the basis of tests for trace amounts of nitroglycerin in air and biological materials, the nitrous acid formed being detected by Griess's reaction. The test may be adapted to the characterization of explosive components in very small samples such as fingernail scrapings.	TLC conditions for separation and detection of nitroglycerin in presence of nitrate esters. Colorimetric visualization.
30	Midkiff, C.R.; Washington, W.D. Systematic Approach to the Detection of Explosive Residues. III. Commercial Dynamite. J. A.O.A.C. 57 (5):1092-1097; 1974.	Tests are described for the detection and identification of suspected dynamite in bombing debris. A discussion of major categories and typical formulations of dynamite is included. Thin layer chromatographic and infrared techniques are utilized for the identification of the explosive oils nitroglycerin and ethylene glycol dinitrate, which are present in most commercial dynamites. Problems encountered with solvent extraction of these oils are discussed. Additional chemical tests performed on the debris to facilitate identification of the particular type of dynamite present in the debris are described.	TLC conditions for separation and identification of nitroglycerin in dynamite residues. Colorimetric visualization. Qualitative identification confirmed by other methods (optical microscopy, GC, IR).
31	Midkiff, C.R.; Washington, W.D. Systematic Approach to the Detection of Explosive Residues. IV. Military Explosives. J. A.O.A.C. 59(6):1357-1974; 1976.	Part IV of the series encompasses tests for the detection and identification of military explosives collected at the scene of a criminal bombing. Major categories and typical formulations of some common military explosives are described. Tests are described and evaluated for the identification of 2,4,6-trinitrotoluene, cyclotrimethylenetrinitramine, and pentaerythritol tetranitrate. Thin layer chromatography and infrared spectroscopy are used for the idetnfication of major explosive components. Tests for minor components to enable characterization and to distinguish similar compositions are included.	TLC conditions for separation and identification of TNT, DNT, RDX and PETN in explosive residues. Colorimetric visualization. Qualitative identification confirmed by other methods (optical microscopy, GC, IR, XRD); spot tests for TNT and RDX performed directly on polyester adhesive tape used to collect particles.
32	Parihar, D.B.; Sharma, S.P.; Verma, K.K. Trace Analysis of Explosives as Pi Complexes. J. Forensic Sci. 13(2):246-252; 1968.	In the detection of explosive advantage may be taken of their highly colored π complexes with aromatic amines. The present paper describes a simple and convenient method for the identification of trace amounts of explosives as charge-transfer complexes with amines employing TLC technique. The resolved π complexes being highly colored could be located easily on the chromatoplates. It was possible to identify as little as 1-2 micrograms of an explosive as its π complex.	The conditions for separation and identification of various explosives. Colorimetric visualization.

TABLE II-1. BIBLIOGRAPHY OF USEFUL CITATIONS (CONTINUED)

ARTICLE NUMBER	REFERENCE	AUTHOR ABSTRACT	COMMENTS
33	Parker, R.G. Analysis of Explosives and Explosive Residues, Part 3: Monomethylamine Nitrate. J. Forensic Sci. 20(2):257-260;1975.	The E.I. duPont de Nemours & Co., Inc., has recently announced that it is discontinuing the manufacturing of nitroglycerin-based dynamites and is replacing them with formulations whose primary ingredients are ammonium nitrate (AN) and monomethylamine nitrate (MMAN). The forensix chemist is thus confronted with the need to be able to analyze residues for the possible use of this type of explosive. In this paper procedures are given for the qualitative determination of MMAN.	TLC used for confirmation of MMAN in presence of various other explosives. Colorimetric visualization.
34	Parker, R.G.; Stephenson, M.O.; McOwen, J.M.; Cherolis, J.A. Analysis of Explosives and Explosive Residues. Part 1: Chemical Tests. J. Forensic Sci. 20(1):133-140; 1975.	In this paper the results of various tests on a select number of ions and organic compounds found in explosives and explosive residues are presented. Any unexplosed explosive particles found by physical examination can be tested by the methods given here.	Spot tests for several explosives of interest. Heating not required for most tests. Tests may be performed on visible particles or solvent extracts. Confirmation by TLC, IR.
35	Parker, R.G.; McOwen, J.M.; Cherolis, J.A. Analysis of Explosive Residues. Part 2: Thin-Layer Chromatography. J. Forensic Sci. 20(2):254-256; 1975.	In Part 1 of this paper the chemical tests used by this laboratory in the screening of explosives and explosive residues were discussed. Part 2 presents the thin-layer chromatographic (TLC) methods used in this laboratory for the confirmation of commonly used organic explosive compounds.	TLC conditions for confirmation of qualitative identification of several explosives of interest. Colorimetric visualization.
36	Peak, S.A. A Thin-Layer Chromatographic Procedure for Confirming the Presence and Identity of Smokeless Powder Flakes. J. Forensic Sci. 25(3):679-681; 1980.	A simple and inexpensive procedure to confirm the identity of unburned or partially burned flakes of smokeless powder is described. The procedure is based on (1) particle morphology and solubility in acetone, (2) R_f values of the flakes when they are chromatographed on thin-layer chromatographic plates, and (3) specificity of the visualizing reagent to nitrite.	TLC conditions for idetnfication of NC in smokeless powder flakes. Physical transfer of visible particles, transfer tape, and culture extraction used for sampling.
37	Pristera, F.; Halik, M.; Castelli, A.; Fredericks, W. Analysis of Explosives Using Infrared Spectroscopy. Anal. Chem. 32(4):495-508; 1960.	A compilation of 68 infrared spectrograms covering all common high-explosive compounds and many possible explosive ingredients, additives, and related compounds has been prepared.	Probably not useful in this study except as confirmatory technique due to 1) relatively large sample size requirement, 2) can be applied only to pure compounds.
38	Sinha, J.K.; Misra, G.J. Projectile Traces. Int. Crim. Police Rev. Series 288:150-151; 1975.	Metallic traces are expected to be retained inside the barrel even after usual cleaning. Therefore, the metallic traces can provide valuable help in determining whether the firearm had ever been fired.	Spot test for lead. Cotton swabs moistened with 25% acetic acid used to obtain samples from gun barrels.
39	Stone, I.C.; Petty, C.S. Examination of Gunshot Residues. J. Forensic Sci. 19(4):784-788; 1974.	The examination of gunshot residues in a forensic science laboratory should be a series of integrated procedures. In this paper we will deal with gunshot residues utilizing soft X-ray radiography, emission spectroscopy (ES), and AAS.	Useful for metals only.

TABLE II-1. BIBLIOGRAPHY OF USEFUL CITATIONS (CONTINUED)

ARTICLE NUMBER	REFERENCE	AUTHOR ABSTRACT	COMMENTS
40	Vouro , P., Petersen, B.A., Colwell, L.; Karger, B.L.; Harris, H. Analysis of Explosives by High Performance Liquid Chromatography and Chemical Ionization Mass Spectrometry. Anal. Chem. 49(7): 1039-1044; 1977.	High performance liquid chromatography and chemical mass spectrometry have been applied to the isolation and identification of explosives. The use of ammonia as a reagent gas for chemical ionization has been evaluated and its advantages over methane, water, hydrogen, and isobutane are discussed on the basis of data from common explosives. The off-line LC-MS approach has been applied to the analysis of simple residues from test explosions under controlled conditions to simulate an actual bombing.	HPLC conditions for separation of NG, RDX, TNT from mixtures. Confirmation by chemical ionization mass spectrometry.
41	Washington, W.D.; Midkiff, C.R. Systematic Approach to the Detection of Explosive Residues. 1. Basic Techniques. J. A.O.A.C. 55(4): 811-822; 1975.	An analysis scheme, in several parts, dealing with the identification of explosives and incendiary destructive devices encountered in actual cases is described. Part I is introductory and is the first step taken in the examination of bomb debris for the various types of explosives and/or incendiaries. Examples and photographs of typical bomb residues are presented.	Recommended approach to identification of trace quantities of homemade, commercial, and military explosives and incendiaries involves 1) optical examination of debris under low magnification for detection of unburned explosive residues, followed by 2) solvent extraction.
42	Washington, W.D.; Midkiff, C.R. Systematic Approach to the Detection of Explosive Residues. J. A.O.A.C. 56(5):1238-	A Vapor Trace Analyzer (VTA) was found to be a valuable tool for scanning bomb debris for traces of certain types of explosives. The application of the VTA in screening bomb debris and locating secreted explosives and uses in other types of physical evidence is discussed. Thin layer chromatography is used to identify physically removed suspected explosive particles and samples from solven extractions of blast material.	Detection of vapors by Vapor Trace Analyzer (VTA) manufactured by Hydronautics-Israel Ltd.; probably not useful in this study except as screening technique because of likely difficulties in quantitation.
43	Yallop, H.J. Breaking Offences with Explosives--The Techniques of the Criminal and the Scientist. J. Forensic Sci. 14:99-102; 1974.	The use of explosives in breaking offences, and in some techniques in the investigation of their use is described.	Recommendation for swabbing of surfaces.
44	Yasuda, S.K. Identification of Impurities in α-Trinitrotoluene by Thin-Layer Chromatography. J. Chromatogr. 13:78-82; 1964.	This article describes a two-dimensional TLC method for the separation and identification of α-TNT impurities, including some oxidation-reduction products of decomposition as well as common production grade impurities. In addition, a unique detection method is described in which the reductor of the developing reagent is directly incorporated in the thin layer.	TLC conditions for several explosives ordinarily occurring as impurities in TNT; colorimetric visualization.
45	Yinon, J.; Zitrin, S. Processing and Interpreting Mass Spectral Data in Forensic Identification of Drugs and Explosives. J. Forensic Sci. 22(4):742-747; 1977.	The value of CI-MS in combination with EI-MS has been demonstrated as an analytical method for the identification of forensic compounds. Data acquisition consists of converting the recorded mass spectra into plotted and tabulated normalized mass spectra by using a central computer. Chemical ionization mass spectral library comparison and identification are done manually.	CI-EI MS of pure compounds and residues; probably not useful in this study except as screening or confirmatory technique.

TABLE II-1. BIBLIOGRAPHY OF USEFUL CITATIONS (CONTINUED)

ARTICLE NUMBER	REFERENCE	AUTHOR ABSTRACT	COMMENTS
46	Bosch, S.F.; Scheuing, D.R. A Rapid Microtechnique for the Detection of Trace Metals from Gunshot Residues. J. Forensic Sci. 21(1): 161-170, 1976.	The use of the Weisz ring oven to localize, concentrate, separate, and identify the four metals of interest from each other and from possible interfering ions and other extraneous matter, is described.	Useful for metals only.
47	Wyant, R.E. Development of a Simple Portable Detection Kit for Selected Explosives. D.T.I.S. Report No. TR-185, September 1977.	An explosive detection spray system has been developed which will detect explosive residues on the exterior of package and letter bombs. The detection is through the formation of colored neutron products using selected spray reagents.	Spot tests for TNT and RDX. Advantage is that tests were performed and evaluated directly on surfaces of interest.

TABLE II-2. ANALYTES DETERMINED IN LISTED CITATIONS

Article Number	Trinitrotoluene (TNT)	Dinitrotoluenes (2,4,- and 2,6-DNT)	Cyclotetramethylenetrinitramine (HMX)	Pentaerythritol tetranitrate (PETN)	Tetryl	Nitroglycerine (NG)	2,4,6-Trinitrophenylmethylnitramine (PICRYL)	Diphenylamine (DPA)	1,3,5-Trinitrobenzene	2,6-Dinitrotoluene	Cadmium (Cd)	Chromium +6 (Cr + 6)	Lead (Pb)	Mercury (Hg)	Chromium +3 (Cr + 3)
1			x												
2	1 ng	2 ng for 2,4-DNT													
3	x	x	x			x									
4															
5		.0025 in THF							.0025 in THF				x		
6	x	x	x	x		x							x		
7	x		x	x			x								
8	x	x							x						
9	1-2 ng		1-2 ng	1-2 ng	1-2 ng		1-2 ng								
10	5-50 ng			5-50 ng		5-50 ng		5-50 ng							
11			Non-specific for nitrate fam.												
12	<2.5 ng	x	x			x	<2.5 ng	x							
13	0.20-1.22 ng		0.17-0.25 ng	0.60-1.23 ng		0.25 ng	0.20-0.87 ng								
14	x		x	500 ng		10 ng	x		x						
15													<8 ng		
16												Total Cr			Total Cr
17															
18	x		x			x									
19	x		x						x						
20	x	x	x	x		x	x								
21															
22	x	x	x	x		x	x		x				0.3 ng		
23															
24				x		x							x		
25															
26													<10 ng		
27													x		
28													51 ng		
29													0.5 ppb in soln.		
30						1 ng									
31	x	x	x	x		x									
32	1.2 ng						1.2 ng								
33	x	x	x	x		x	x								
34	x	x	x	x		x	x								
35	x	x	x	x		x	x								
36						x									
37	x	x	x	x		x	x		x						
38															x
39															x
40	x		1 ng			x									
41															
42		Qualitative for polar compounds													
43															
44	x	x							x						
45	x														
46														Total Cr .05 ng	.05 ng
47	0.1 ng		0.5 ng												

TABLE II-3. ANALYTICAL METHODS DESCRIBED IN LISTED CITATIONS

Article Number	Classification	Microscopic Methods		Classical Wet Chemical Methods		Chromatographic Methods			Absorption Spectroscopic Methods		Atomic Spectroscopic Methods		X Ray Methods		Mass Spectrometric Methods		Other		
	Method	Optical Microscopy	S.E.M.	Spot Tests	Ring-Oven Technique	TLC	GC	HPLC	IR	UV	AAS	AES	XRD	XRF	CI-MS	EI-MS	ASV	INAA	Photo Isothermography
1				■															
2				■															
3				■															
4			■																
5							■												
6		■		■		■			■			■	■						
7													■						
8						■													
9									■										
10						■													
11				■															
12								■											
13						■													
14						■													
15																	■		
16																		■	
17											■								
18		■		■		■	■		■										
19							■												
20						■													
21																			■
22						■	■		■	■									
23														■					
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29						■													
30		■				■	■		■										
31		■		■		■	■		■										
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36						■													
37									■										
38				■															
39											■								
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41		■																	
42							■												
43																			
44						■													
45																			
46					■														
47				■															

Abbreviations: S.E.M. = Scanning Electron Microscope
TLC = Thin Layer Chromatography
GC = Gas Chromatography
HPLC = High Performance Liquid Chromatography
IR = Infrared Spectroscopy
UV = Ultraviolet Spectroscopy
AAS = Atomic Absorption Spectroscopy
AES = Atomic Emission Spectroscopy
XRD = X-ray Diffraction
XRF = X-ray Fluorescence
CI-MS = Chemical Ionization Mass Spectrometry
EI-MS = Electron Impact Mass Spectrometry
ASV = Anodic Stripping Voltammetry
INAA = Neutron Activation Analysis

TABLE II-4. SAMPLING AND SAMPLE PREPARATION PROCEDURES DESCRIBED IN LISTED CITATIONS

Article No.	Sampling Procedure	Sample Preparation	Interferences
1	Standard samples.	Mix sample and rgts.; heat	Pale blue-green color of cyclotetramethylenetetranitramine (HMX) may be distinguished from RDX by repeating test at 150°C; RDX is the only ampd. commonly found in explosive formulations that gives a blue color in this test.
2	Standard samples.	Mix sample and rgts.	In the presence of NG, color produced with DNT is green; initial color should be observed since changes occur with time.
3	Cotton wool swabs soaked with ether, water.		
4	Sellotape transparent adhesive tape used for physical transfer of particles from skin.	Mix sample and rgts.	
5	Extraction with hexane.		
6	Extract residue with ether, acetone.	Spot sample soln. on TLC plate, develop.	
7	Physical transfer of residue crystal from surface.	None.	
8	Acetone solution of process sample.		
9	Standard samples.	KBr pellet.	
10	Collect vapors on short column containing porous polymer beads.	Extract column with acetone, concentrate.	
11	Paraffin cast of hands of persons known or suspected to have discharged firearms.		
12	Synthetic mixtures.	Mix rgts.	NO_3^- ion
13	Not specified.		
14	Physical transfer of explosive fragments from surface.	Spot sample soln. on TLC plate.	
15	Hands of persons known to have discharged firearms were cleaned with filter paper moistened with HNO_3.	Spot sample soln. on TLC plate, develop.	
16	Surface sample analyzed directly.	Ash filter; dissolve residue.	
17	Cotton swab, film-lifting with films made from solns. of film-forming polymers, transparent adhesive tape.	Ash collection medium, dissolve residue.	
18	Physical transfer of explosive fragments from surface, solvent extraction, cotton-wool swabs.		

TABLE II-4. SAMPLING AND SAMPLE PREPARATION PROCEDURES DESCRIBED IN LISTED CITATIONS (CONTINUED)

Article No.	Sampling Procedure	Sample Preparation	Interferences
19	Standard samples.	Sample soln. spotted on TLC plate, developed; resolved spot removed from plate by scraping, extracted, resulting soln. analyzed by GC.	
20	Solvent extraction; cotton v l swabs soakded in appropriate solvent used for extraction of compounds from hands and clothing.		
21	Distilled water wash of hands.	Spot sample on TLC plate, develop.	
22	Extraction with hot acetone, hot water.		
23	Direct analysis.	Method dependent.	
24	Cotton swabs soaked in acetone.		
25	Wash hand in 1 M HCl.	Spot sample soln. on TLC plate, develop.	
26	Wash hand in 1 M HNO_3.		Cadmium
27	Wash hand in (1) detergent (2) 0.5 M HCl.		
28	Standard samples.		
29	Dissolve material in acetone.	Add 0.1 M acetate buffer to sample soln.	
30	Extraction with chloroform, acetone.	Spot sample soln. on TLC plate, develop.	
31	Extraction with chlorof acetone; for hands, cotton swabs moistened with acetone or polyester film adhesive tape.	Spot sample soln. on TLC plate, develop.	
32	Standard samples in acetone solution.	Spot sample soln. on TLC plate, develop.	
33	Standard solns. in water.	Spot sample soln. on TLC plate, develop.	
34	Extraction with acetone.	Mix sample and rgts.	Extractions material. Substitute methane or ether for acetone in extraction step or take up residue from acetone extraction with these solvents.
35	Extraction with acetone.	Spot sample soln. on TLC plate, develop.	

TABLE II-4. SAMPLING AND SAMPLE PREPARATION PROCEDURES DESCRIBED IN LISTED CITATIONS (CONTINUED)

Article No.	Sampling Procedure	Sample Preparation	Interferences
36	Physical transfer of visible profiles, transfer tape, or culture extraction.	Place profile or spot sample soln. on TLC plate, develop.	
37	Standard samples.		
38	Cotton swabs moistened with 25% acetic acid.	Add rgts. to swab, observe color.	
39	For cloth, extraction with HNO_3; for hands, swabbing with HNO_3, HCl.		
40	Standard samples; acetone extraction.		
41	Optical examination under low magnification, solvent extraction.		
42	Detection of vapors.		
43	Swabs.		
44	Standard samples in chloroform.	Spot sample soln. on TLC plate, develop.	
45	Direct analysis of residue obtained after evaporation of solvent from acetone extract.		
46	1:1 HCl extraction	Place sample soln. on filter paper, wet, spot test residues.	
47	Spray reagents directly on surface.		

C. REVIEW OF SPOT TEST CHARACTERISTICS:

At the request of the Technical Project Officer, a review of the spot tests used for detection of explosives/explosive residues was carried out concurrent with the literature search to determine whether those tests could be used for in-situ detection of explosives on the surface types of interest in this study.

Tables II-5 through II-8 list and describe selected characteristics of spot tests which may affect their suitability for use for qualitative analysis of explosives/explosive residues on the surface types of interest. Tables II-5 and II-6 list spot test methods and characteristics by analyte. Tables II-7 and II-8 list spot test methods by reagents used in the respective methods, and list and describe selected properties and characteristics which may be exhibited by those reagents when used under the conditions specified in the method.

To evaluate the data included in these tables, we defined a set of minimum criteria which a spot test proposed for use for the contemplated qualitative analysis should satisfy. These criteria were: (1) the spot test should permit rapid screening of large areas; (2) it should be sensitive down to the agreed upon detection limit of 0.5 µg of analyte/cm^2 under various surface conditions; (3) it should be specific for the analyte of interest; (4) it should not result in an irreversible chemical reaction which would make the analyte unavailable for subsequent quantitative testing; (5) its use should not present an unusual hazard to the operator due to the toxicity, flammability, or other hazardous characteristics of reagents, reaction products, or reaction conditions, and; (6) it should not result in a net increase in the amount of contamination present in and on the surface tested and should not in any other way affect the suitability of that surface for any projected future use.

The overall finding of this evaluation based on the available data was that there is no single spot test or combination of a few such tests which satisfies all of these criteria. More significantly, most available spot tests typically fail totally to meet one or more of these criteria. It is possible that modifications could be made to available tests to improve their performance in this regard. However, the developmental effort required for that purpose may be substantial, and it is not clear that improvement in the performance of a given spot test with respect to one criterion would be accompanied by similar improvement in other areas.

In summary, our view is that available spot tests do not satisfy minimum criteria for qualitative analysis of explosives/explosive residues on building material surfaces. We do not recommend that developmental effort be expended on spot test methods except for those analytes or conditions for which no more- or equally-promising methods can be identified and developed.

Notes for Colorimetric Spot Test Tables

Literature numbers:

1 through 47 correspond to journal articles 1 through 47 listed in Table II-1.

F_1 is Feigl, F. and Anger, V. Spot Tests in Inorganic Analysis, Elsevier Publishing Co., Amsterdam (1972) (6th English Edition).

F_2 is Feigl, F. and Anger, V. Spot Tests in Organic Analysis, Elsevier Publishing Co., Amsterdam (1966) (7th English Edition).

(a) is Christensen, H.E. and Luginbyhl, T.T. (eds) Toxic Substances List: 1974 Edition, U.S. Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Health and Safety, Rockville, Maryland, June (1974).

(b) is Sax, I.N. Dangerous Properties of Industrial Materials, Reinhold Book Corporation, New York (1968).

(c) is International Technical Information Institute (ITI) Toxic and Hazardous: Industrial Chemicals Safety Manual, Tokyo (1976).

Abbreviations:

cat - cat
dog - dog
gpg - guinea pig
hmn - human
inh - inhalation
ipr - intraperitoneal
ivn - intravenous
LD50 - lowest dose 50% kill
LDLo - lowest published lethal dose
LC50 - lethal concentration 50% kill
LDLo - lowest published lethal concentration
mky - monkey
mus - mouse
orl - oral
rat - rat
rbt - rabbit
scu - subcutaneous
TVL - threshhold limit value; the concentration of an airborne constituent to which workers may be exposed repeatedly without adverse effects.

TABLE II-5. SPOT TEST METHODS FOR ORGANIC ANALYTES

Analyte	Reagent	Solvent	Lit. No.	Color	Threshold	Interferences	Technique and Sampling
Cyclotrimethylene trinitramine (RDX)	Thymol	Ethanol Sulfuric acid	1 3 18 31	Cold → red Strong heat → yellow/brown Moderate heat → violet Add ethanol → Blue		HMX (heat will separate); Many sugars and aldehydes; 4 out of 24 tested nitramines	Heating required; test tube
	J-acid (0.4%)	95% ethanol; Add a few seconds later	31 34	Yellow-red first; then with ethanol → blue → blue/green → gray		Nitrates others	Tape removes sample; spot plate
	Brucine		34	Orange to red		Bromide, Chlorate, Nitrate, Nitrite, Nitroglycerin, Nitrocellulose, Nitrostarch, Tetryl, PETN	Spot plate
	Griess		34	Pink to red		Bromide, Chlorate, Nitrate, Nitrite, Nitroglycerin, Tetryl, Nitrocellulose, Nitrostarch, PETN	Spot plate
	Procaine - N N'-dimethyl-1-naphthylamine	50/50 acetic acid/H_2O 10 gm zinc in 100 ml benzene	47	Red/red-violet λ = 530/535 ε = 42,330/45,477	Sometimes 40 μg; usually 4 μg or 0.4 μg	Glue on paper envelopes; PETN, nitroglycerin; nitrites	On wood (glue) gives too color - threshold 40.0 μg; on papers - 0.4 μg
	Alizarin	40 ml concentrated Sulfuric acid	F_2	Yellow		HMX Nitrates Nitramines	Spot plate
2,4 dinitrophenol	50 mg zinc dust	Hot alcohol 10% $CaCl_2$ $Na_3[Fe(CN)_5NH_3]$	F_2	Violet		TNT 2,4 DNT 1,3,5 trinitrobenzene; other nitro compounds	Heating required; test tube
	KCN	2N HCl (later)	F_2	Red	1γ	m-dinitro compounds	Micro crucible

TABLE II-5. SPOT TEST METHODS FOR ORGANIC ANALYTES (CONTINUED)

Analyte	Reagent	Solvent	Lit. No.	Color	Threshold	Interferences	Technique and Sampling
2,4-DNT	25% aqueous tetramethylammonium hydroxide	Acetone-alcohol	2	Blue (changes over time)	2 µg	None in standard explosive residue	Spot plate
	Saturated potassium hydroxide	Ethyl alcohol	18 31	Deep red		Not tetracene PETN RDX HMX	White spot plate; samples taken from soil, concrete and rubble
	50 mg. zinc dust	Hot alcohol 10% $CuCl_2$ $Na_3[Fe(CN)_5NH_3]$	F_2	Violet		TNT 1,3,5 trinitrobenzene 2,4 dinitrophenol nitro compounds	Test tube
	0.3% 1-naphthylamine	.5% sulfanic acid 1N alkali alcohol acetic acid	F_2	Red		TNT 2,6 DNT trinitrobenzene other aromatic polynitro compounds	Micro test tube
2,6 DNT	.3% 1-naphthylamine	.5% sulfanic acid 1N alkali alcohol acetic acid	F_2	Red		TNT 2,4 DNT trinitrobenzene other aromatic polynitro compounds	Micro test tube
Diphenylamine	5% phosphomolybdic acid	Concentrated ammonia	F_2	Blue to blue/green	.1 γ	Large number of organics phenol resorcinol aniline naphthylamine	Spot plate
	$KClO_3$	Concentrated HCl ether 1% tetralose	F_2	Blue	.25 γ	Many aromatic compounds	Micro test tube
	2,4-dinitrochlorobenzene	Ether	F_2	Yellow	1.6 γ	Various amine bases aniline piperidine tetralose	Spot plate
	Thiodiphenylamine	Ether methanolic bromine	F_2	Blue	10 γ	dialkylamines aralkylamines Various secondary amines	Test tube
	0.05% p-nitrosophenol	HCl	F_2	Blue	0.1 γ	Various analgous compounds	Spot plate

TABLE II-5. SPOT TEST METHODS FOR ORGANIC ANALYTES (CONTINUED)

Analyte	Reagent	Solvent	Lit. No.	Color	Threshhold	Interferences	Technique and Sampling
TNT	25% aqueous Tetramethylammonium Hydroxide	Acetone Alcohol	2	Dark red (changes with time)	1 µg	None found in explosives residue	Spot plate
	Nessler's reagent	Absolute alcohol	3 6 34	Red		Aldehyde Thio compounds Alkali sulfides Organic solvents (acetone, methanol, ethanol)	Spot plate
	Saturated potassium hydroxide	Ethyl alcohol	18 31	Deep red		Not tetracene PETN RDX HMX	White spot plate (samples taken from soil, concrete, rubble)
	1,3 diphenyl-acetone Et_4-NOH	Ethanol	47	Red-red/orange λ = 500/503 ϵ = 32,270/22,272	0.4 µg on paper	Polynitro aromatic compounds	Tested on papers, wood, cloth, leather
	Cyclopentanone Et_4-NOH	Ethanol	47	Red λ = 511/512 ϵ = 10,445/22,272	0.4 µg on paper		Wood > tan color; detection limit 4.0 µg
	Nitromethane Et_4-NOH	Ethanol	47	Red-orange λ = 505/505 ϵ = 28,510/22,272	0.4 µg on paper		Wood > tan color; detection limit 4.0 µg
	Zinc dust (50 mg)	Hot alcohol 10% $CaCl_2$ $Na_3[Fe(CN)_5NH_3]$	F_2	Violet		2,4 DNT 2,4 dinitrophenol 1,3,5 trinitrobenzene Other nitro compounds	Test tube
	.3% 1-naphthylamine	.5% sulfanic acid IN alkali alcohol acetic acid	F_2	Red		TNT 2,4 DNT 2,6 DNT 1,3,5 trinitrobenzene Other aromatic polynitro compounds	Micro test tube
	1,2-naphthoquinone -4-sulfonate	50% alcohol dilute NaOH	F_2	Brown-red		Compounds containing reactive CH_2 and NH_2 groups	Micro crucible

TABLE II-5. SPOT TEST METHODS FOR ORGANIC ANALYTES (CONTINUED)

Analyte	Reagent	Solvent	Lit. No.	Color	Threshhold	Interferences	Technique and Sampling
PETN	Diphenylamine	Sulfuric acid	31	Deep blue		Nitrates	Tape sample; Spot plate
	Modified Griess reagent	.1g sulfanic acid	31 34	Red		Nitrates Tetryl RDX NC	Tape sample; Spot plate
	Brucine	Acetone	34	Orange-red		Bromide Chlorate Nitrite NC Nitrocellulose RDX Nitrostarch Tetryl	Spot plate
	Procaine N-N'-dimethyl-1-naphthylamine	50/50 acetic acid/H_2O 10g zinc dust 100 ml benzene	47	Red-red/violet λ = 530/535 ϵ = 42,333/42,770	0.4 µg on paper	Nitrites RDX NC	On wood + tan color; 4.0 µg detection limit
1,3,5 tri-nitrobenzene	50 mg zinc dust	Hot alcohol 10% $CaCl_2$ $Na_3[Fe(CN)_5NH_3]$	F_2	Violet		TNT 2,4 DNT 2,4 dinitrophenol Other nitro compounds	Test tube
	.1% 1-naphthylamine	.5% sulfanic acid 1N alkali alcohol acetic acid	F_2	Red		TNT 2,4 DNT 2,6 DNT Dinitrophenol Other aromatic polynitro compounds	Micro test tube

TABLE II-5. SPOT TEST METHODS FOR ORGANIC ANALYTES (CONTINUED)

Analyte	Reagent	Solvent	Lit. No.	Color	Threshhold	Interferences	Technique and Sampling
NG: nitroglycerin	Nessler's reagent	Absolute alcohol ammonia	3 34 6	Yellow → orange/brown ammonia → black	2 mg	Aldehydes, thio compounds, alkali sulfides, organic solvents (acetone, methanol, ethanol)	Sample off cotton swabs in ether; sample removed from rubble; white spot plate
	Brucine	Acetone	34	Orange-red		Bromine, Chlorate, Iodine, Nitrate, Nitrite, Nitrocellulose, Nitrostarch, PETN, Tetryl, RDX	Extraction with acetone; Spot plate
	Diphenylamine	Acetone	34	Blue-blue/black		Chlorate, Nitrate, Nitrite, Nitrocellulose, Nitrostarch, PETN, Tetryl	Extraction with acetone; Spot plate
	Griess	Acetone	34	Pink to red		Nitrate, Nitrite, Nitrocellulose, RDX, PETN, Tetryl	Extraction with acetone; Spot plate
	1-acid	Acetone	34	Orange-brown		Bromine, Chlorate, Iodine, Nitrate, Nitrocellulose, PETN, Nitrostarch, RDX, Tetryl	Extraction with acetone; Spot plate
	Nitron		34	Light, dirty-white precipitate		Chlorate, Iodine, Nitrite, Perchlorate	Spot plate
	Procaine N,N' diethyl-1-naphthylamine	50/50 acetic acid/H_2O Zinc dust (10 g) Benzene (100 ml)	47	Red-red/violet λ = 530/535 ϵ = 42,333/42,770	0.4 µg usually	Nitrite, RDX, PETN	On wood only 4.0 µg detection; rest on paper

TABLE II-6. REAGENTS FOR ORGANIC ANALYTES

Reagent	Solvent	Analyte	Lit. No.	Practicability			Hazard		
				Destructiveness	Application	Simplicity	Toxicity	Flammability	Danger
Benzene		PETN NG RDX	47				Suspected carcinogen; TLV (ACGIH rec) 25 ppm in air 80 mg/m^3 in air (b) TLV = 10 ppm Inhalation TCLo=210ppm (c)	Flammable Rigorous reaction with heat (b)	Face shield; breathing apparatus; Safety goggles (c)
Brucine 5 g brucine sulfate	100 ml concentrated sulfuric acid	PETN RDX NG	34	Acid chars organics			High (b) Inhalation highly toxic; Ipr-rat LD_{50}=77 $\frac{mg}{kg}$ Ivn-rbt LDLo=30 $\frac{mg}{kg}$ (c)	Heat + toxic fumes (b)	Rubber gloves; Work in draft protective clothing; Respirator; (c)
Chloranil (tetrachloro-benzoquinone)	Ether $KClO_3$ $HClO_3$	Diphenyl-amine	F_2	Redox reaction		Requires air-drying, warming.	See benzoquinone: Ipr-rat LD50 = 7510 $\frac{mg}{kg}$ (b)	Heat + toxic fumes (b)	
Cyclopentanone Et_4NI	Ethanol	TNT	47				LD50 = 4490 $\frac{mg}{kg}$ LDLo = 302 mg/kg (a) Cycloparaffins: deadly narcotic (b)	Moderate flammable (b)	
2,4-dinitro-chlorobenzene	Ether	Diphenyl-amine	F_2	Forms quinoidal zwitterion condensation products			Moderate to high skin irritant (b) ori-rat LD_{50} = 1070 $\frac{mg}{kg}$ skn-rbt LD50 = 130 $\frac{mg}{kg}$	Slight (b)	Moderate explosive when exposed to flame (b) shock or heat explosive (c)
1,3 Diphenyl-acetone Et_4NOH	Ethanol	TNT	47			Commercially available	LDLo = 102 $\frac{mg}{kg}$ (a)		
Diphenylamine	100 ml concentrated sulphonic acid acetone methanol	PETN	31	Acid clears organics		Is also an analyte	LDLo = ~200 $\frac{mg}{kg}$ LDLo = 102 mg/kg (a)		Explosive

TABLE II-6. REAGENTS FOR ORGANIC ANALYTES (CONTINUED)

Reagent	Solvent	Analyte	Lit. No.	Practicability			Hazard		
				Destructiveness	Application	Simplicity	Toxicity	Flammability	Danger
Phosphomolybdic acid (5%)	Ammonia	Diphenylamine	F_2	redox reaction					
Potasium cyanide	2N HCl (later)	2,4 dinitrophenol	F_2	Presumed product: phenylhydoxylamines		Requires heating	Skin irritant toxic (b)	Moderate flammable, emits hydrocyanic acid on heating; highly toxic gas (b)	
Potasium hydroxide	Ethyl alcohol	TNT 2,4-DNT	18 31				orl-rat LD50=365 $\frac{mg}{kg}$ (c) highly toxic for inhalation (b)	reacts with water or steam to produce caustic solution - toxic (b)	Corrosive liquid (b) rubber gloves face shield (c)
Procaine (.35 gm) N,N'-dimethyl-1-naphthylamine (.35 gm)	50-50 acetic acid - H_2O 10 gm Zn dust Benzene (100 ml)	PETN NG RDX	47				LD50=500 mg/kg LD50 =1400 mg/kg (a)	Moderate heat > toxic fumes (b)	Explosive under shock or heat (b)
Quinalizarin (3 mg) (1,2,5,8-tetrahydroxyanthraquinone)	40 ml concentrated sulfuric acid	RDX	F_2	Nitric acid splits off	Stir 20 sec; wait 20 min. precisely				
25% aqueous tetramethylammonium hydroxide	acetone alcohol	TNT m-dinitrobenzene 2-4 DNT	2			Clear mobile liquid	Toxic - powerful caustic (b)		Corrosive liquid (b)
Thymol	Sulfuric acid Ethanol	RDX	1	Acid chars organic		Requires heating to 100°C	Slight toxicity (b) orl rat LD50=900 $\frac{mg}{kg}$ orl-mus LD50=1800 $\frac{mg}{kg}$ orl gpg LD50=800 $\frac{mg}{kg}$ (c)	Toxic fumes upon heating (b) Flammable (c)	Rubber gloves face shield gas mask (c)

TABLE II-6. REAGENTS FOR ORGANIC ANALYTES (CONTINUED)

Reagent	Solvent	Analyte	Lit. No.	Practicability			Hazard		
				Destructiveness	Application	Simplicity	Toxicity	Flammability	Danger
Griess reagent (α-naphthylamine) (1-naphthylamine)	0.5% sulfanic acid 1N alkali alcohol acetic acid	2,4 di-nitro-phenol; TNT; 2,4 DNT; 2,6 DNT; 1,3,5 tri-nitro-benzene; PETN; RDX	31 34 F_2	Ar – NO_2 goes to Ar – OK		Reagent lasts 2 months if refrigerated	LD_{50} ~2 g/kg LDLo=150 mg/kg (a) Highly toxic, bladder cancer (b) orl-rat LD50=779 $\frac{mg}{kg}$ scu-mus TDLO=25 $\frac{mg}{kg}$ scu-dog TDLO=400 $\frac{mg}{kg}$ (c)	Slight heat + toxic fumes (b)	Monthly urine analysis necessary (c)
J-acid (6-amino-1-naphthol sulfonic acid)	95% ethanol	RDX	31 34	Acid chars organics					
1,2-naphtho-quinone-4-sulfonate	50% alcohol dilute NaOH	TNT	F_2	Forms: indophenol dye					
Nessler's Reagent (KI) ($HgCl_2$) (KOH)	Alcohol	NG TNT	3 4				KI: Prolonged absorption →iodism, skin rash (b)	Heated → toxic iodine fumes. (b)	
Nitromethane	Ethanol	TNT	47				LD50 = 940 mg/kg LDLo = 102 mg/kg (a) Highly toxic TLV (ACGIH rec) 100 ppm in air 250 $\mu g/m^3$ in air (b) Inhl mky LCLo=2446 $\frac{mg}{m^3}$ (c)		Explosive store away from heat; rubber gloves, respirator, plastic clothes (c)
Nitron	88% formic acid	NG	34						
p-nitrosophenol	HCl	diphenyl-amine	F_2	Oxidized to meriquinoidal compounds			May resemble p-nitrophol; if so, high toxicity (b)		Highly explosive when exposed to flame (b)

TABLE II-7. SPOT TEST METHODS FOR INORGANIC ANALYTES

Analyte	Reagent	Solvent	Lit. No.	Color	Threshhold	Interferences	Technique and Sampling
Cd	$Fe(\alpha,\alpha'\text{-dip}_3)_2$		F_1	Red	.05γ	Metal ions and Cu^{+2}, Hg, Sn, Sb If reagent treated with ammonia, only Ag and Tl interfer	Filter paper
Cd	Di-p-nitrophenyl-carbazide	Formaldehyde 10% NaOH 10% KCN Alcohol	F_1	Brown → green/blue	.08γ		Spot plate
Cd	Glyoxal bis-(2-hydroxyanil)	Piperidine alcohol 20% sodium thiosulfate 20% sodium tartrate Saturated sodium fluoride	F_1	Blue	.05γ		Spot plate
Cr^{+3}	Chenta acid		F_1	Reddish violet	Microgram amounts	Cu, Co, Ni Not Cr^{+6}	Heated in boiling water bath for 5 minutes Spot plate
Cr^{+3}	Acid Alizarin RC	Heated 2N H_2SO_4	F_1	Orange-yellow → greenish	.06γ	Not Group III Metals	Filter paper
Cr^{+6}	Alkali hypobromate	Concentrated H_2SO_4 20% Sulfosalicylic acid	F_1	Violet	.25γ	Cu^{+2}, Co^{+2}, Ni^{+2} Fe^{+3}	Spot plate
Cr^{+6}	Benzidine	Moderate concentration sodium peroxide Acetic acid	F_1	Blue	.25γ		Filter paper
Pb	o-dinitrobenzene	Alcohol 0.5N caustic alkali	F_1	Violet		Metals Al etc...	Micro test tube boiling water
Pb	0.02% Sodium rhodizonate	25% Acetic acid	38	Pink			Gun barrel swab Spot plate

TABLE II-8. REAGENTS FOR INORGANIC ANALYTES

Reagent	Solvent	Analyte	Lit. No.	Practicability			Hazard		
				Destructiveness	Application	Simplicity	Toxicity	Flammability	Danger
cid Alizarin 3G	Hexed 2N H_2SO_4	Cr^{+3}	F_1		Cannot be washed out of paper with H_2O or acids	Requires heating			
Alkali hypobromate	Concentrated H_2SO_4 10% sulfosalicylic acid	Cr^{+6}	F_1	Forms CrO_4^{-2}					
Benzidine	Sodium peroxide Acetic acid	Cr^{+6}	F_1	Oxidized to chromate			-Any exposure extremely hazardous; poison label (b) -Carcinogen ori-dog LDLo 100 mg/kg (c)	-Heat = decomposition hazardous fumes (b)	-Rubber gloves; plastic overalls; self-contained breathing apparatus (c)
ienzoic acid ,2-diamino-cyclohexane-,N,N',N'-tetraacetic cid)		Cr^{+3}	F_1			Requires boiling water bath			
3-dinitrobenze	Alcohol 0.5N caustic alkali	Pb	F_1	Forms alkali salt of quinoidal nitrol-nitro acid			m-dinitrobenzene: TLV = 1 mg/m_3 ori-cat LDLo = 27 mg/kg (c)	m-dinitrobenzene: slight	m-dinitrobenze: High explosive hazard (b) Special outdoor storage advised (c) Rubber gloves; breathing apparatus (c)
-p-nitrophenyl- arsonate	10% NaOH 10% KCN 40% formaldehyde	Cd	F_1	Forms $Cd(OH)_2$					
(aa'-dip)$_3I_2$ -dipyridyl $FeSO_4$ KI	Ammonia	Cd	F_1	Forms CdI_2			For aa'dipyridyl see pyridine (b) Pyridine: TLV = 5 ppm in air (b)	Pyridine: heat = decomposition, hazardous fumes, highly flammable (b)	Pyridine: explosive vapors special storage (c) rubber gloves(c) breathing apparatus
Glyoxal bis-(2-hydroxyanil)		Cd	F_1	Forms a colored chelate		Requires beads of resin	Glyoxal: moderate (b) ori-rat LDLo = 100 mg/kg (c)	Glyoxal: slight (b)	Glyoxal: rubber gloves breathing apparatus (c)
Sodium rhodizonate	Acetic acid	Pb	38						

D. FINDINGS AND CONCLUSIONS:

Among the overall findings of the literature search and spot test review are the following:

- The literature search indicates that most of the prior work in this area has been done by law enforcement agencies, and those agencies have, for the most part, concentrated on the application of spot test methods for the detection of explosives: quantitative determination of explosives has not been a major concern, except to the extent that these investigators have attempted to demonstrate the range of concentrations to which their qualitative detection methods could be applied. The Army, also, has relied mainly on spot test methods up to now in explosives contamination assessment work. However, as noted above, available spot tests do not satisfy minimum criteria for qualitative analysis of explosives/explosive residues on building material surfaces.

- Other investigators have reported explosives determination techniques involving analytical methods ranging in sophistication from visual examination of residue under low power magnification to mass spectrometry, including in between almost all readily available modern analytical techniques. Sampling for quantitative analysis remains a weak spot. Thus, different methods for qualitative and quantitative analysis may be required to satisfy the Army's requirements.

- The use of a qualitative survey obviously must not preclude the subsequent use of a quantitative method if two different methods are used for qualitative and quantitative analysis, application of the qualitative method should not result in the destruction or loss of analyte. Many of the methods described in articles collected in the literature review result in loss or destruction of analyte and thus may not be applicable to the present problem.

- Recommended sampling and analytical methods should not result in a net increase in the amount of contamination through the application of toxic or hazardous reagents to the surface to be tested, nor should they present any other hazard to the operator. Many of the materials described in the literature review require the use of toxic reagents and thus for this reason also may not be applicable to the present problem.

- Surface contamination of the type the Army is concerned with is most likely to have resulted from spillage or dusting of solids or from spillage of process liquors or liquid wastes. The latter situation presents the problem of sampling compounds which may have penetrated into porous surfaces such as wood or concrete. Most existing methods do not address this issue.

E. SAMPLING PROTOCOL SELECTION:

Based on the review of the available literature and discussions with the Technical Project Officer and other persons having expertise in trace analysis and explosives technology, the following sampling protocols were identified as candidates for developmental testing:

1. continuous monitoring of organic analyte vapors using a portable gas chromatograph;

2. evaluation of existing U.S. Army equipment developed for the vapor phase detection of CW agents;

3. in-situ formation of charge-transfer complexes with visual identification;

4. UV irradiation of suspected contaminated surfaces with subsequent detection based on thermal imaging or UV photography of the irradiated surface;

5. Solvent extraction using alternative procedures to conventional wipe or swab methods.

Protocols 1, 2, 3, and 4 were candidates for qualitative detection of explosives/explosives residues; protocol 5, combined with modified versions of existing USATHAMA methods for the determination of explosives was intended for quantitative determination. Detailed discussions of the developmental testing of these qualitative and quantitative methods are presented in the respective sections of this report.

III. QUALITATIVE METHODS DEVELOPMENT

A. INTRODUCTION:

The qualitative methods selected for developmental testing included:

1. continuous monitoring of organic analyte vapors using a portable gas chromatograph;

2. evaluation of existing U.S. Army equipment developed for the vapor phase detection of CW agents;

3. in-situ formation of change-transfer complexes with visual identification;

4. UV irradiation of suspected contaminated surfaces with subsequent detection based on thermal imaging or UV photography.

Detailed discussions of the developmental testing of these methods are presented in the respective sections below.

The objective of this testing was development of procedures for the rapid qualitative determination with 90% confidence of the presence/absence of the compounds of interest down to a level of 5 $\mu g/10\ cm^2$ in a given building. The approach used to achieve this objective involved in each case the spiking with known amounts of analytes of new, uncontaminated samples of each of the surface types of interest obtained from building materials dealers. Samples of conductive non-sparking flooring were not available for this purpose.

Practical determination of the confidence interval associated with a qualitative analysis performed in the field would have required access to a building where the nature and extent of contamination was known. This condition could not be satisfied by those AAP's to which access was obtained. Therefore, detection limits for positive compound identification are reported.

At the direction of the Technical Project Officer, emphasis was placed on the development of procedures for organic analytes. No methods for inorganic species which would represent substantive improvement over existing spot test methods were finally identified.

B. ANALYTE DETECTION USING CONTINUOUS VAPOR PHASE MONITORING:

The detection of explosive vapors using gas chromatography and other analytical techniques has been the object of considerable investigative effort. In fact, several of the commercially-available explosives detectors are based on this principle. Available explosives vapor detection methods have been used with varying degrees of success for the detection of bulk explosives as, for example, in airport and aircraft security operations.

Detection of explosives/explosive residues on building materials surfaces using continuous vapor phase monitoring could offer the following advantages:

- By means of one or a few measurements, all the surfaces composing an entire enclosed area could be effectively screened for the presence of explosives;
- The analyses could be performed on or close to a real-time basis, making it possible to conduct "walk-through" surveys.

Unfortunately, however, there are several potential difficulties with using continuous vapor phase monitoring for detection of explosives on surfaces, including the following:

- The concentrations of analytes on surfaces which are of interest in this study are very low;
- Further, the vapor pressures of most of the analytes of interest are very low under ambient conditions;
- Most of the analytes of interest are strongly polar and thus adsorb strongly on surfaces with which they come in contact.

These factors have, in fact, largely precluded the effective use of vapor phase detection methods for many applications where the detection of other than bulk quantities of explosives was attempted.

Two types of recently-developed analytical instruments were evaluated in this study to determine whether their operating and performance characteristics made possible the detection of vapors derived from explosives in air immediately adjacent to surfaces spiked with explosives/explosive residues. One was the Photovac 10A10 Portable Gas Chromatograph (Photovac, Inc., Thornhill, Ontario, Canada), a portable gas chromatograph with a photoionization detector for which detection levels down to parts per billion for various compounds including nitro-compounds are claimed. A technical representative of Photovac, Inc. visited Arthur D. Little, Inc. laboratories to discuss the application of the Photovac 10A10 Portable Gas Chromatograph to continuous monitoring of organic explosive vapors and to demonstrate the performance of that instrument used in its continuous monitoring mode for sampling of air immediately above a surface spiked with known amounds of selected explosives. During that demonstration, the Photovac 10A10 failed to give any observable signal when used to sample the air immediately above the bottoms of Pyrex glass beakers spiked with the equivalent of 125 $\mu g/cm^2$ of RDX, 2,4-DNT, and DPA.

The Arthur D. Little, Inc. Project Manager and the Technical Project Officer also visited U.S. Army C.S.L. Laboratories to view and assess the performance of U.S. Army CW agent field detection equipment when used to sample explosives vapors. Three ionization detectors, including the model in current use and two prototype instruments, were evaluated by sampling the air immediately above the bottoms of Pyrex glass beakers spiked with various concentrations of RDX, 2,4-DNT, and DPA. Each of the detectors gave what appeared to be an observable response at or near the agreed-upon detection

limit of 0.5 $\mu g/cm^2$. However, in no case was that response sufficiently large to assure unambiguous detection. It was judged that none of these instruments appears at this time to possess sufficient sensitivity to warrant further investigation in this project.

C. ANALYTE DETECTION USING FORMATION OF CHARGE TRANFER COMPLEXES WITH VISUAL IDENTIFICATION:

1. Background.

Charge-transfer complexes, particularly molecular addition compounds, have been used for years in the isolation, purification and identification of organic compounds. Among the better known examples are the addition compounds of 2,4,6-trinitrophenol (picric acid), 1,3,5-trinitrobenzene and 2,4,7-trinitrofluorenone. These nitroaromatic compounds are charge-transfer "electron-acceptors." Their complexes with "electron-donors" are usually formed in 1:1 ratios of acceptor:donor, and the combination exhibits properties differing from the individual components, e.g., color, crystal structure, melting point, etc. The bond strength of the addition compounds varies from very weak--on the order of van der Waal's forces--to moderate strength such as in hydrogen bonding. The simple aromatic hydrocarbons, e.g., durene, naphthalene, and anthracene, are typical donor compounds whose complexes have the weaker type of bonds such that the solid complexes can be readily dissociated by loss of the donor through volatilization at or only slightly above room temperature. Solvent action can also be used to remove the donor compound from the complex.

In the interaction of nitroaromatic hydrocarbons with the simpler aromatic materials, visible color due to complex formation would be the simplest method of detection. In the absence of a good color contrast, the known property of nitroaromatics to quench the fluorescence of the other aromatic compounds could be used as the basis for a less simple detection scheme. Of the donor compounds mentioned above, however, only anthracene has a fluorescence at visible wave lengths such that it could be used without an instrumental detector. Still another combination of a physico-chemical interaction of a fluorescent donor with the quenching nitroaromatic acceptor compound as part of an energy-transfer system might also be used to increase the sensitivity of detection. Work performed by Arthur D. Little, Inc. on detection of polycyclic aromatic hydrocarbons indicates that less than nanogram quantities of anthracene can be detected by virtue of that compound's energized fluorescence. The interference of nitro-aromatic compounds with such a test should thus permit their detection at a corresponding level (cf. Interagency Energy/Environmental Report EPA 600/7-78-182, September 1978).

In summary, in-situ formation of charge-transfer complexes for the detection of explosives on building materials surfaces offers the following advantages:

(1) Sensitivity down to the desired detection limit of 0.5 μg of analyte/cm^2;

(2) Speed: the chemical reactions used in this application occur under ambient conditions; relatively easy and straightforward methods for dispersal of the required reagents over large areas of the surface types of interest are available; and visual observation of colors or quenching is used as the detection method;

(3) Manageable hazard during and subsequent to use as compared to similar spot test methods; and

(4) Reversibility: the charge-transfer complexes used in this application can be destroyed relatively easily leaving the original analyte intact and available for subsequent quantitative testing.

2. Preliminary Experiments

Whatman No. 42 filter paper was used as a substrate in place of samples of the actual surface types of interest in initial spiking experiments. Filter paper or the equivalent is customarily used in this type of work since it provides a convenient means for manipulating the small amounts of chemicals involved and also provides a nearly ideal visual background for visualizing the colors or fluorescence of reaction products.

Acetonitrile solutions of three of the organic analytes--2,4,6-TNT, 2,4-DNT, and RDX--were applied to Whatman No. 42 filter paper in quantities sufficient to yield concentrations equivalent to 0.5 μg and 50 μg of analyte/cm^2 (= 1x and 10x the agreed-upon detection limit of 0.5 μg/cm^2). The acetonitrile was allowed to evaporate, and the spiked filter paper was then treated with cotton swabs which had been immersed in acetonitrile solutions containing 100 μg/mL of the electron-donor compounds durene, hexamethylbenzene, naphthalene, and anthracene.

The filter paper was then examined for (1) the presence of colored reaction products, or (2) quenching of reagent fluorescence when examined under a UV lamp. First priority was assigned to identifying a reagent which gave a colored reaction product which, at all concentrations, was clearly visible to the unaided eye under ambient lighting conditions and was clearly distinguishable from any potentially interfering colors or surface irregularities. Detection of a reaction by observation of quenching of reagent fluorescence was considered acceptable only if a colored reaction product could be identified; in that case, the observed quenching should satisfy the same criteria as above.

In an effort to identify an electron-donor compound which would yield a colored reaction product with these analytes, the compounds N,N-dimethylaniline and diphenylamine were also evaluated using the procedures described above. While diphenylamine is also an analyte in this program, it was nevertheless considered useful to evaluate its electron-donor properties since it is often cited in the literature as a strong electron-donor and could thus serve as a useful model compound.

At the 50 $\mu g/cm^2$ level, 2,4,6-TNT formed a reddish-orange spot with both N,N-dimethylaniline and diphenylamine; 2,4-DNT formed a pale yellow spot with diphenylamine only; and RDX failed to form an observable colored spot with either compound. At the 0.5 $\mu g/cm^2$ level, none of the analytes formed an observable colored spot with either compound. However, when spiked filter paper treated with anthracene was observed under ultraviolet illumination (254 nm), quenching of the anthracene fluorescence was observed for all analytes at both concentrations.

On the basis of these initial positive findings, additional experiments were performed on the nine analytes listed below:

Analytes Tested

NG	Nitroglycerin
PETN	Pentaerythritetetranitrate
RDX	Cyclotrimethylenetrinitramine
TNT	2,4,6-trinitrotoluene
TNB	1,3,5-trinitrobenzene
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
DNP	2,4-dinitrophenol
Tetryl	2,4,6-trinitrophenylmethylnitramine

Each analyte was spiked on Whatman No. 42 paper at levels corresponding to 0.5, 1.0 and 100X the specified detection limit (0.5 $\mu g/cm^2$). As in the preceding experiments, cotton swabs which had been immersed in an acetonitrile solution containing 100 ug/mL of anthracene was gently drawn across the filter paper. After the acetonitrile had evaporated, the paper was examined under 254 nm UV illumination.

All of the analytes except NG and PETN were detected at the 100X level without application of anthracene; the detections were as dark spots on the light paper background. (In visible white light, the DNP and Tetryl spots were yellow.) When treated with anthracene, all of the analyte spots were seen as dark spots on the fluorescent anthracene background.

At the 1X (0.5 $\mu g/cm^2$) level, again only NG and PETN spots were not evident until treated with anthracene. Even at this level, they did show a weak quench of the anthracene fluorescence. The other compounds, evident without anthracene, showed increased contrast (dark/white) with the reagent.

At the 1/2X (0.25 $\mu g/cm^2$) level, none of the materials were detected until treated with anthracene. PETN, NG, and RDX detections are questionable at that level. Taken together, these findings suggested that detection of the three analytes tested at the agreed-upon detection limit of 0.5 $\mu g/cm^2$ was well within the capabilities of the technique.

3. Formation of Charge-Transfer Complexes Directly on Surfaces.

In an additional set of experiments, analytes were spiked directly on clean samples of the surface types of interest. The acetonitrile/anthracene solution was sprayed on the spiked surface sample using a spray bottle. In each case in which the quenching of the anthracene was positively identified, a lower concentration of the analyte was spiked on a clean sample of the surface type being examined on the experiment repeated. The lowest concentration at which quenching of the anthracene fluorescence could be positively identified was taken as the detection limit for that analyte-surface combination. The resulting detection limits are listed in Table III-1.

An additional finding of this work was that several spray applications (i.e., 3-4) of the anthracene/naphthalene reagent are necessary to achieve a uniform fluorescence background on brick and concrete. With a single application of reagent, surface irregularities appear as slightly darker areas and cannot be distinguished from analyte.

It was also observed in these experiments that the presence of dirt or other foreign matter on metal and wood surfaces prevented uniform spreading of the reagent over the surface. Also, care is required on metal and wood surfaces to avoid puddling or running of the reagent, which may result in removal from or dilution within the area being examined of any analyte present.

4. Solvent Lift Technique for Sampling of Surfaces.

The analyte detection limits shown in Table III-1 are higher for all analyte-surface combinations than for the same analytes on filter paper. In an effort to determine whether lower detection limits could be obtained, alternative procedures for isolating the analyte from a surface prior to treatment with the acetonitrile/anthracene solution were evaluated.

TABLE III-1. LABORATORY ANALYTE DETECTION LIMITS (MICROGRAM/cm^2) OBTAINED BY FORMATION OF CHARGE TRANSFER COMPLEXES DIRECTLY ON SURFACES

Analyte	Surface				
	Metal[1,2]	Concrete	Transite	Brick	Wood[2]
NG	500	320	45[3]	50	240
PETN	500	320	45[3]	50	400
RDX	500	320	144[3]	160	400
TNT	600[4]	320	30[4]	160	240
TNB	42	320[4]	30[4]	160[4]	160
2,4-DNT	13	100	14	50[4]	160
2,6-DNT	13	100	14	50[4]	96
DNP	42[4]	100[5]	30[4]	50	96[5]
Tetryl	42[4]	320[4,5]	30	50	160[5]

[1]All analytes could be seen at the reported concentrations with the unaided eye as crystals on the metal surfaces.

[2]Wood and metal surfaces were precleaned with acetone to assure uniform spreading of reagent.

[3]No increase in the analyte/background contrast was observed at analyte concentrations up to 300 $\mu g/cm^2$.

[4]Reported concentrations are for positive identification: analytes <u>may</u> be seen at lower concentrations.

[5]DNP and Tetryl could be seen at the reported concentrations with the unaided eye as yellow stains.

The best results were obtained using the following procedures: 1) Whatman No. 42 9.0 cm filter paper circles were saturated with 0.5-10 mL acetonitrile; 2) the wetted filter paper was pressed against the surface of interest; 3) the filter paper was allowed to remain in place until the acetonitrile had evaporated; 4) the filter paper was removed and stored in 100 x 15 mm disposable plastic Petri dishes (Fisher Scienctific Co. Cat. No. 8-757-12) until analyzed.

Using these procedures, the detection limits are shown in Table III-2 were obtained. Comparison of these results to those in Table III-1 indicates that the detection limits obtained using the solvent lift technique are lower in almost all cases than those obtained by formation and detection of charge-transfer complexes directly on surfaces. The solvent/lift approach also eliminates the analyte dilution and reagent puddling problems which may accompany the accidental application of excess reagent.

5. Field Evaluation.

During the week of April 19, 1982, visits were made to Holston Army Ammunition Plant in Kingsport, Tennessee and Joliet Army Ammunition Plant in Joliet, Illinois to evaluate under field conditions the charge-transfer complex formation solvent lift sampling protocol described above. A total of 195 filter paper lift samples were collected at the two installations using the procedures described above. Seventy filter paper lift samples were obtained at Holston AAP and 125 were obtained at Joliet AAP. Six locations in five different buildings at the two installations were sampled in this manner. Solid samples were also collected from four buildings at the two installations. In each case, the specific locations sampled were those which personnel familiar with present or former manufacturing processes performed at these installations suspected were contaminated with the explosives of interest. A complete inventory of all samples is included in Table III-3.

The variety of buildings and locations sampled represents most of the sampling conditions likely to be encountered in the field. It was noted, however, that even among nominally identical manufacturing lines and buildings at a given installation, substantial differences were encountered between equipment types and configurations, previous types and of intensities of usage, etc. The significance of this observation is that the development of a generalized sampling plan would probably not be possible or useful.

Due to safety restrictions and the absence of readily accessible AC power supplies, only a few filter paper lift samples were analyzed in the field for demonstration purposes. In all other respects, however, the filter paper lift approach proved to be easy and efficient to use. All samples were returned to Arthur D. Little, Inc. laboratories and were analyzed within two weeks. Several samples which were suspected to be contaminated with explosives were reanalyzed at various times over

TABLE III-2. LABORATORY ANALYTE DETECTION LIMITS (MICROGRAMS/cm^2) USING SOLVENT LIFT TECHNIQUE

Analyte	Surface				
	Metal	Concrete	Transite	Brick	Wood
RDX	50	100	50	100	0.5
TNT	5	50	50	50	0.5
2,4-DNT	5	50	5	50	0.5
2,6-DNT	5	50	50	50	0.5
Tetryl	5	100	5	50	0.5

TABLE III-3. INVENTORY OF SAMPLES COLLECTED AT HOLSTON AND JOLIET ARMY AMMUNITION PLANTS

Site	Building	Area	Sample No.	Sample Type
Holston	1	top of wooden drain cover	1 2 3 4	filter paper lift
Holston	I1	bottom of wooden drain cover	5 6 7 8	filter paper lift
Holston	I1	bottom of concrete drain basin	9 10 11	filter paper lift
Holston	I1	wall frame base (wooden)	12 13	filter paper lift
Holston	I1	metal wall frame	14 15	filter paper lift
Holston	I1	base of concrete wall	16 17	filter paper lift
Holston	I1	two feet from floor on concrete wall	18	filter paper lift
Holston	I1	corner of concrete floor	19 20	filter paper lift
Holston	I1	one foot from floor on a concrete wall	21 22 23 24 25 26 27	filter paper lift
Holston	I1	bottom of wooden door frame	28	filter paper lift
Holston	I1	one foot up on a concrete wall	29 30 31 32 33	filter paper lift

TABLE III-3. INVENTORY OF SAMPLES COLLECTED AT HOLSTON AND JOLIET ARMY AMMUNITION PLANTS (CONTINUED)

Site	Building	Area	Sample No.	Sample Type
Holston	I1	concrete floor (area covered 15 1/2' x 14')	34 + 55	filter paper
Holston	I1	concrete pump base	56 + 63	filter paper lift
Holston	I1	metal strip a long face of pump base	64 65 66	filter paper lift
Holston	I1	drain basin pump base	67 68S 69S 70S	white powder concrete concrete concrete
Holston	D_4 (RDX reaction building)	flooring wall baseboard door frame tank base equipment base pump base pump base wall base drain base	71S 72S 73S 74S 75S 76S 77S 78S 79S 80S	asphalte brick tar material wood white powder material concrete concrete concrete black tar material black powder
Joliet	TNT shell loading	second floor melting bay area (concrete)	101 + 162	filter paper lift
Joliet	TNT shell loading	first floor loading bay (concrete)	163 + 186	filter paper lift
Joliet	DNT sweathouse	first floor drain area (concrete)	187 + 194	filter paper lift
Joliet	DNT sweathouse	transite wall paneling	200 + 204	filter paper lift
Joliet	TNT washhouse	concrete floor	205 + 209	filter paper lift

TABLE III-3. INVENTORY OF SAMPLES COLLECTED AT HOLSTON AND JOLIET ARMY AMMUNITION PLANTS (CONTINUED)

Site	Building	Area	Sample No.	Sample Type
Joliet	TNT washhouse	concrete sump basin	210 + 213	filter paper lift
Joliet	Tetryl packaging	non sparking floor	216 217 218	filter paper lift
Joliet	Tetryl packaging	concrete drain basin	219 + 222	filter paper lift
Joliet	Tetryl packaging	non sparking floor	223	filter paper lift
Joleit	Tetryl	sheet metal dust collector	224 225	filter paper lift
Joliet	TNT unloading	second floor flooring	3015	wood floor covering
Joliet	Tetryl packaging	floor	3025	non sparking floor
Joliet	Tetryl	drain basin	3035	white powder

an additional two-week period and in each case the observed results were indistinguishable, indicating that no observable loss of analyte occurred upon storage of samples for up to one month.

The solid sample 675 collected from a floor drain in Building I-1 at Holston AAP was analyzed separately by x-ray diffraction and was found to consist mainly of RDX. Acetonitrile washes of several filter paper lift samples collected from the same general area were also analyzed independently by a wet chemical method for identification of RDX (ref. Dept. of the Army Technical Manual TM 9-1300-214, Military Explosives, No. 1967, p. 12-4) and were found to give positive results for that analyte. Several additional filter paper lift samples from nearby areas which contained amounts of dirt and debris similar in quantity and appearance to that on the samples described above gave no indication of contamination. Taken together, these observations suggest that certain of the areas sampled in Building I-1 at Holston AAP were indeed contaminated with RDX, that the charge-transfer complex formation sampling protocol gave a positive indication of contamination in and around areas where contamination was known to exist, and, in areas further removed from the known contaminated areas, the charge-transfer sampling protocol gave fewer or no indications of contamination. The latter observation, in particular, suggests that the presence of dirt and debris of the type found throughout the building did not result in false positive findings. This is precisely the outcome which had been desired.

The results of analyses of all filter lift samples are represented diagramatically in Figures III-1 through III-6. In those figures, small circles indicate the locations from which filter paper lift samples were collected. Open circles ○ represent a finding of no apparent explosives contamination; crossed circles ⊕ represent a finding that the location sampled was contaminated with explosives. Findings which were questionable due to very faint fluorescnece are denoted by the appropriate notation next to the corresponding location in the figure.

D. ANALYTE DETECTION USING UV IRRADIATION AND THERMAL IMAGING:

1. Background.

An analytical approach utilizing UV irradiation and thermal imaging technology was evaluated for its potential applicability to the detection of trace levels of explosives on building materials surfaces. The principles underlying this approach involved the following:

The area of interest is irradiated with an ultraviolet illumination source matched to the absorption characteristics of the analyte. The radiation that is absorbed must necessarily heat the material. A small change in temperature should result and thermal imaging technology might be used to sense that change in temperature, provided that diffusion of the heat into the substrate does not proceed too rapidly.

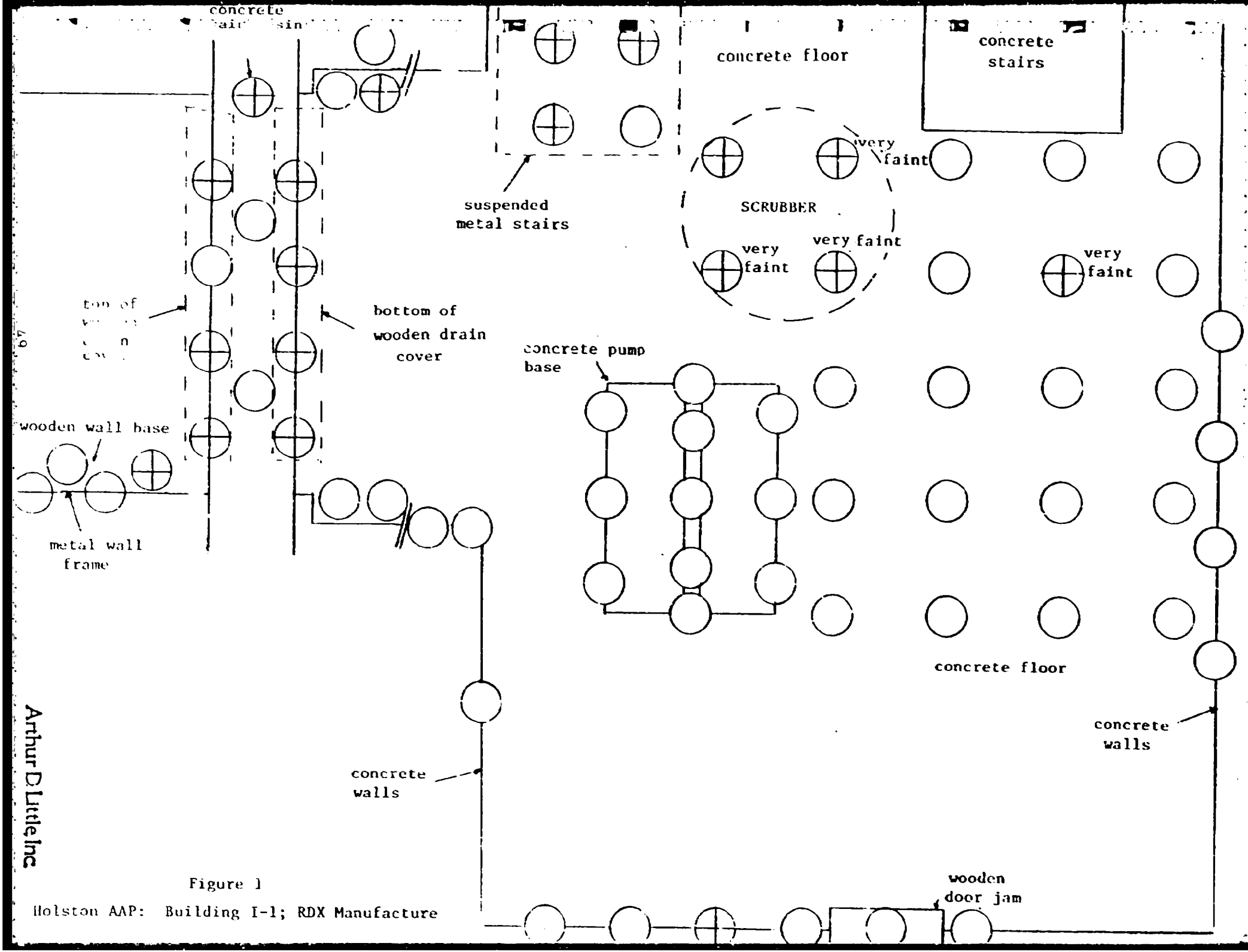


Figure 1

Holston AAP: Building I-1; RDX Manufacture

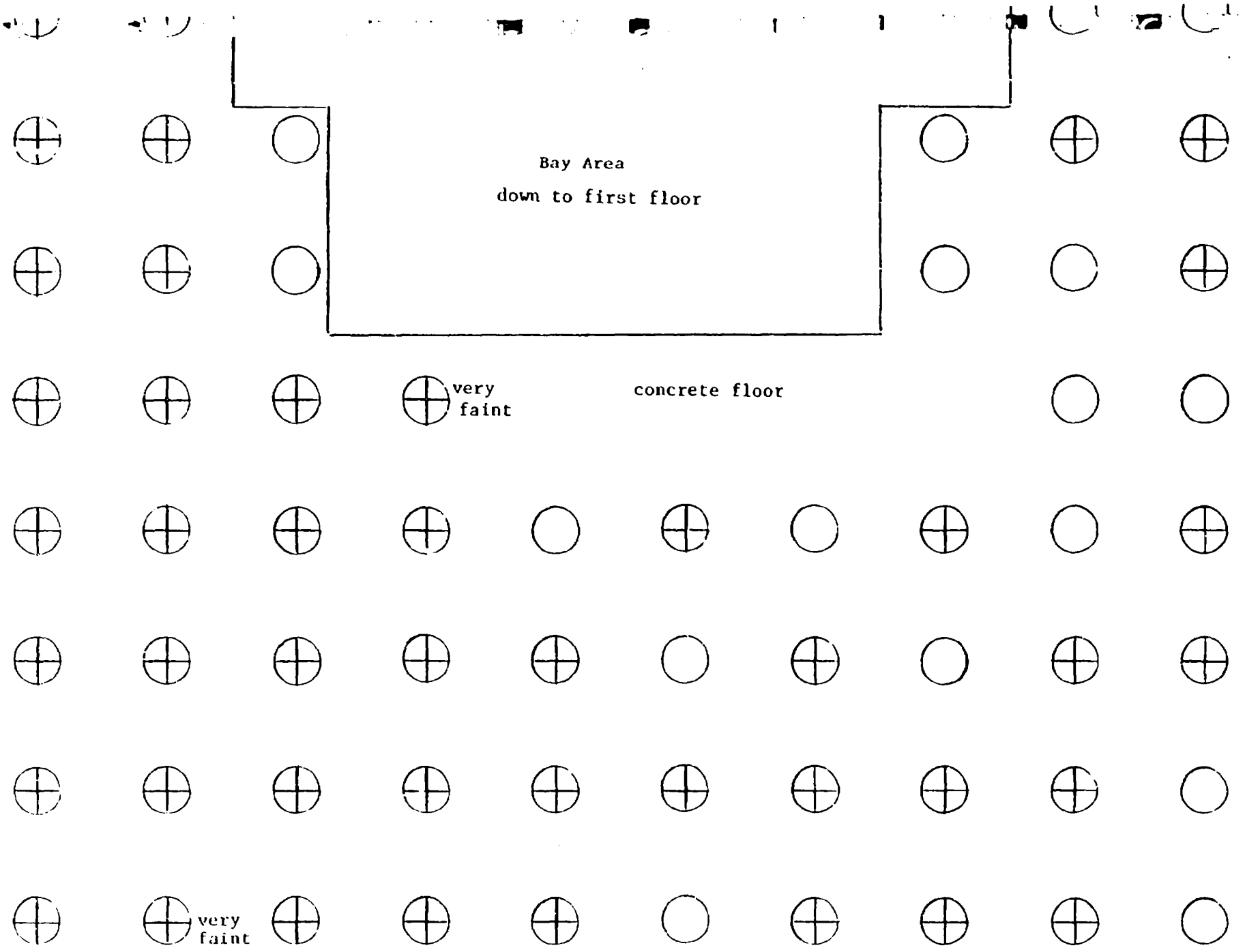


Figure 2

Joliet AAP: TNT Melting Area, 2nd Floor

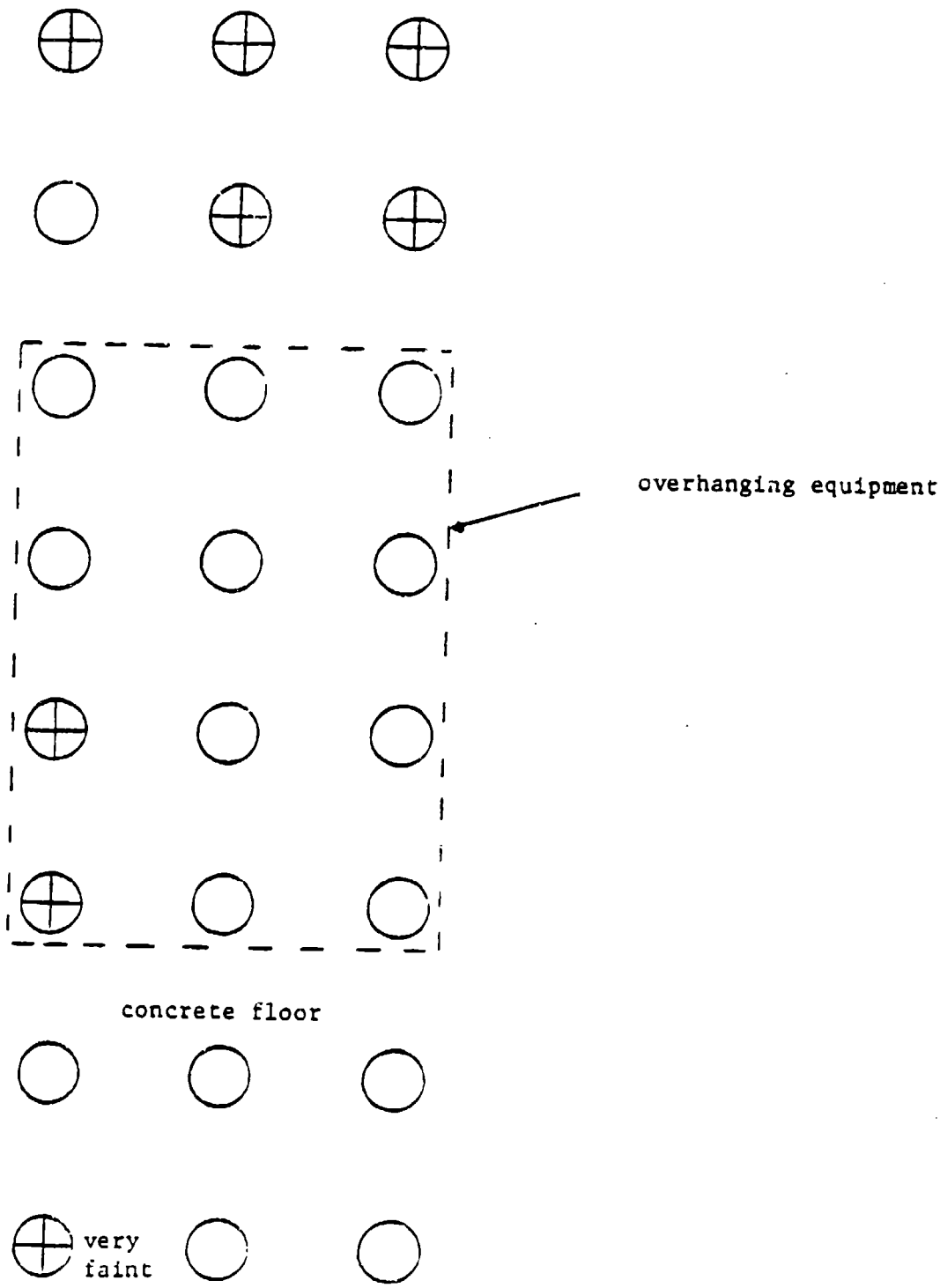


Figure III-3

Joliet AAAP: TNT Loading Area, 1st Floor

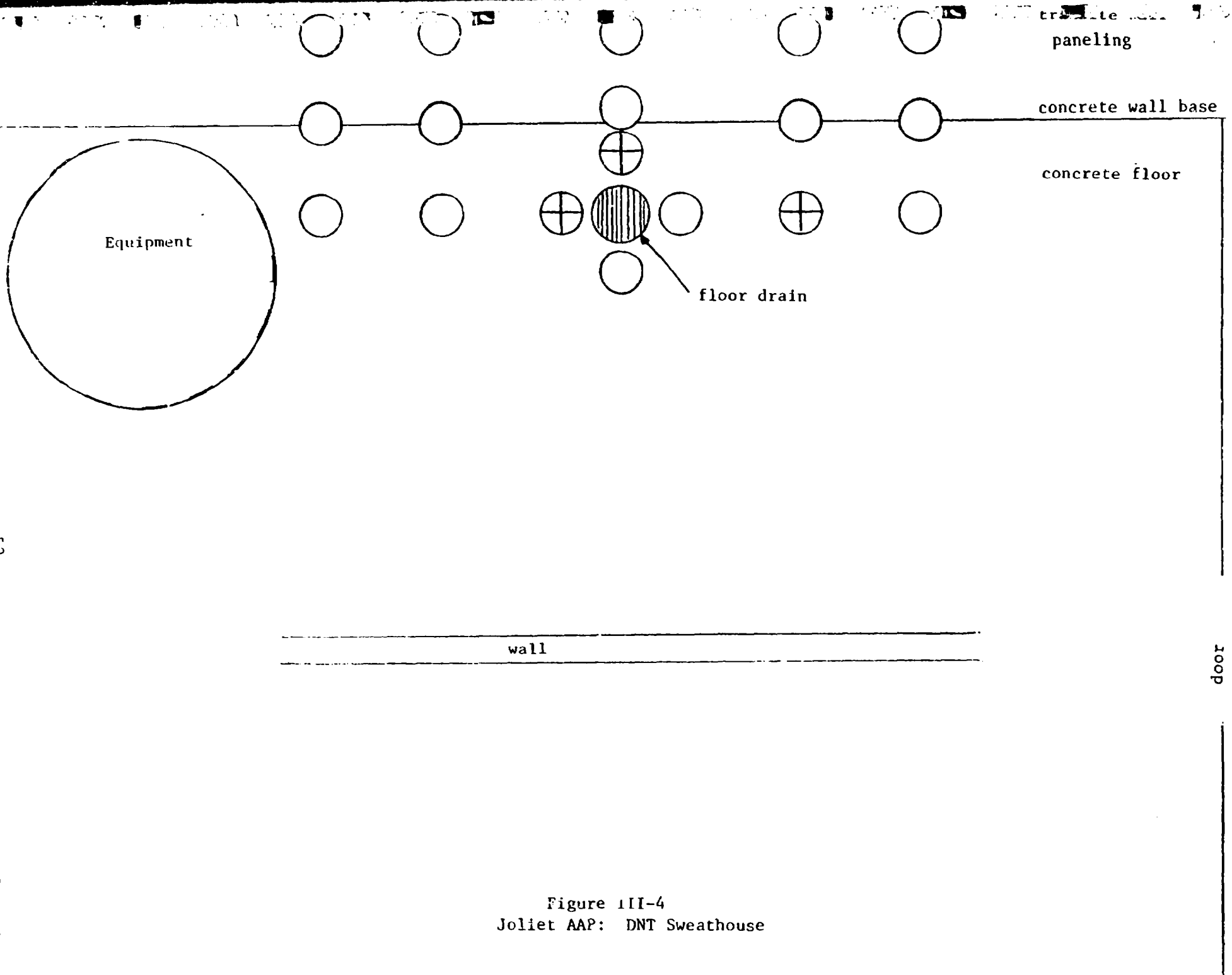


Figure III-4
Joliet AAP: DNT Sweathouse

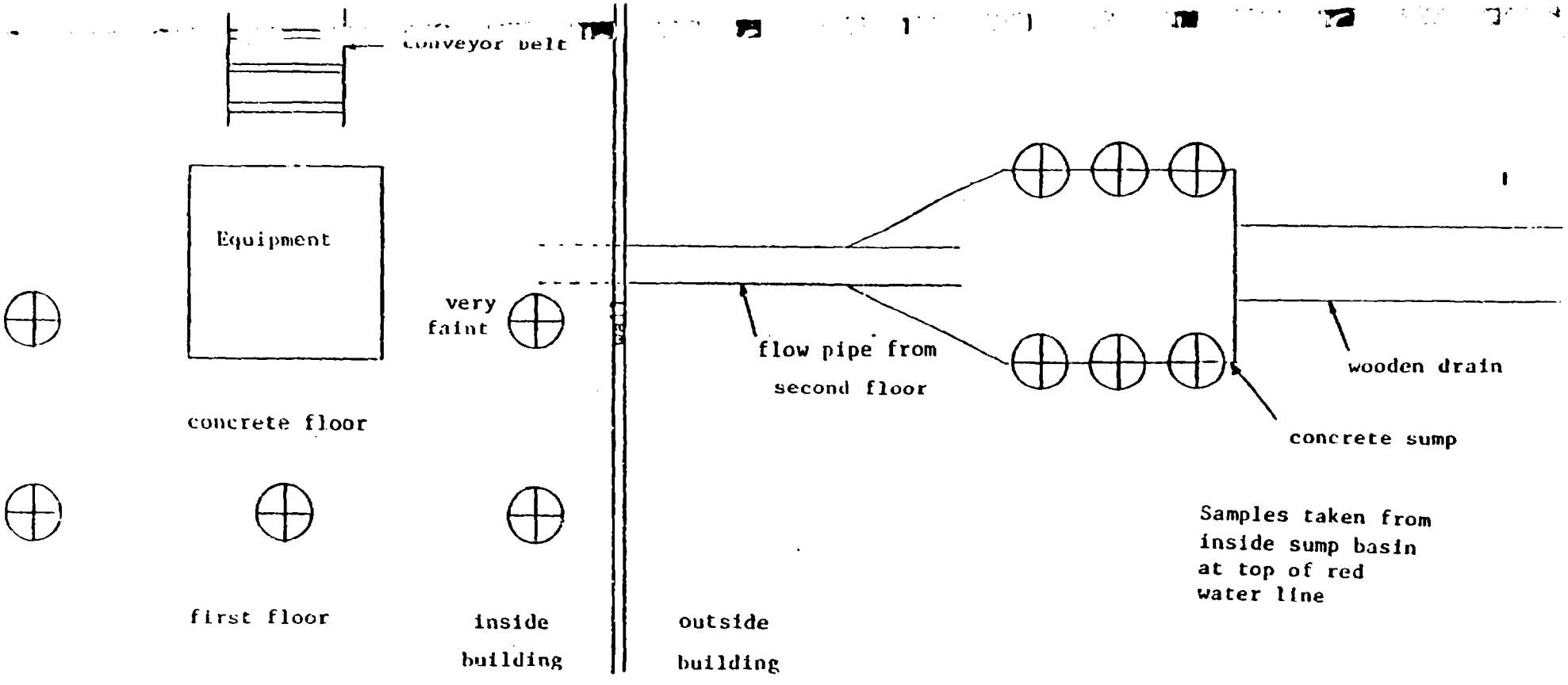


Figure III-5

Joliet AAP: TNT Wash Building

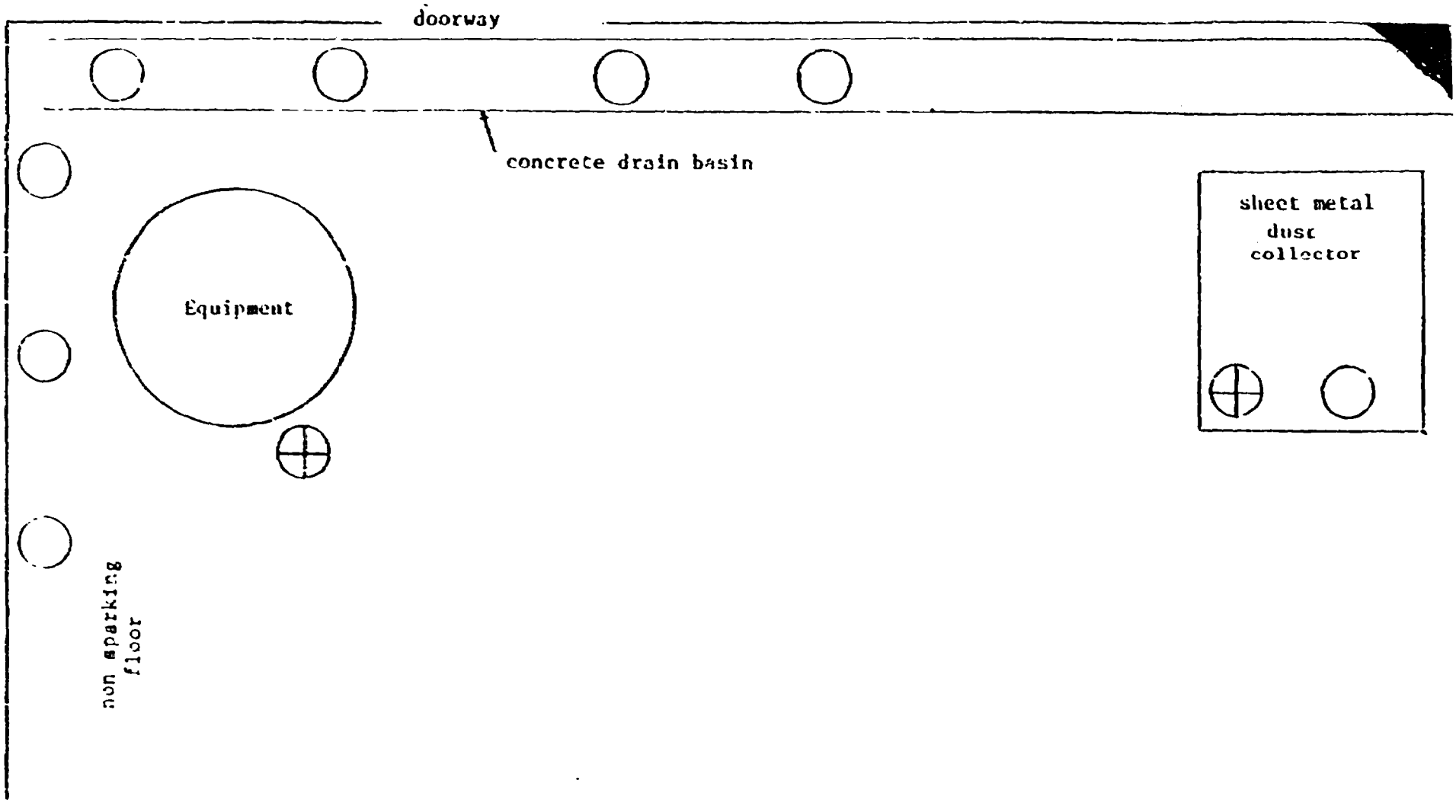


Figure III-6

Joliet AAP: Tetryl Packaging Building

The technical feasibility of this approach was evaluated by a theoretical analysis which showed that the estimated temperature increases accompanying UV irradiation of trace levels of the analytes on surfaces were apparently within the measurement capabilities of commercially available thermal imaging instrumentation. Subsequent laboratory experiments demonstrated the practical applicability of the approach. The work completed in each of these steps is summarized in the respective sections below.

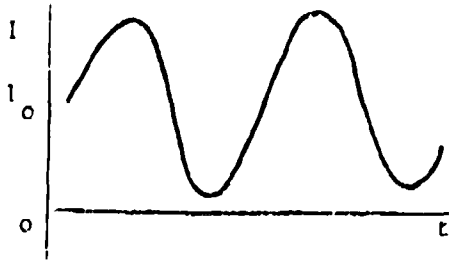
2. Theoretical Analysis of the Method.

a. Principle. The explosives of interest are known to have absorption bands in the middle IR and in the UV but are not fluorescent in the UV. Thus, irradiation of these compounds with UV or IR light of the proper wavelength will result in energy absorption accompanied by a rise in temperature. That temperature rise may provide the means for detecting the presence of the explosives on building materials surfaces. Because modern instrumentation is capable of precise measurement of even very small temperature changes (e.g., $\Delta T = 0.1°C$), the method may be extended to the detection of trace levels of explosives. Discrimination of analyte signal from background temperature fluctuations can, in theory, be achieved by careful selection of the incident radiation.

A detection method based on this principle would involve illuminating the wall with UV irradiation of specific wavelengths tuned to the suspected material's absorption bands and sensing the temperature rise due to the absorbed radiation. The absorption coefficients are generally so much greater in the UV than in the IR that a UV method is to be preferred. To maximize the temperature rise, one could illuminate the wall with a narrow beam of radiation which slowly scanned the wall. The temperature rise can be sensed by a thermal-infrared detector that scans the wall in synchronism with the illuminating beam. The illuminating beam can be either chopped or unmodulated. Because the observed temperature change may be strongly dependent on which beam type is chosen, both methods will be examined.

b. Chopped-Radiation Methods

By means of a suitable chopper, the incident radiation intensity, I, as a function of time, t, can be made to have the form shown below:



Chopped Incident Radiation as a Function of Time

This function can be represented by the formula

$$I = \tfrac{1}{2} I_o \ (1 + \cos \omega t) \tag{1}$$

consisting of a steady component

$$I_s = \tfrac{1}{2} I_o \tag{2}$$

and an alternating component

$$I_a = \tfrac{1}{2} I_o \ e^{i\omega t} \tag{3}$$

where for mathematical convenience we have replaced cos ωt by $e^{i\omega t}$.

If a lock-in amplifier tuned to the angular frequency ω is used with the detector, only the effect of the component I_a is observed. It is to be noted that since I_a takes on both positive and negative values, this component of the intensity implies formally that power is both put into and taken out of the wall.

If the thin absorbing layer is of thickness d and absorption coefficient α, at the wavelength of the incident beam, the intensity transmitted through the layer is

$$I_t = (1-R) \ I_a \ e^{-\alpha d} = \frac{(1-R)}{2} \ I_o \ e^{-\alpha d} \ e^{i\omega t} \tag{4}$$

where R is the reflectance of the film at the irradiation wavelength and the power per unit area absorbed in the layer is therefore

$$W = \frac{(1-R)}{2} \ I_o \ (1 - e^{-\alpha d}) \tag{5}$$

where the factor $e^{i\omega t}$ has been suppressed.

We assume that the transmitted intensity, given by Equation (4), is slowly absorbed by the underlying wall and therefore does not appreciably affect the temperature distribution set up in the wall.

The temperature distribution in the wall is given by the heat flow equation

$$K \frac{\partial^2 T}{\partial x^2} = C \ \rho \ \frac{\partial T}{\partial t} = i\omega \ C \ \rho \ T \tag{6}$$

where x is distance into the wall, and K, C, ρ are, respectively, the thermal conductivity, specific heat and density of the wall material.

The solution of Equation 6 is

$$T = T_o\, e^{-\sqrt{\frac{i\omega}{k}}\, x} \tag{7}$$

where k is the thermal diffusivity, given by

$$k = \frac{K}{C\,\rho} \tag{8}$$

and T_o is the surface-temperature amplitude.

The heat flux density at x = p is

$$q = -K \left(\frac{\partial T}{\partial x} \right)_{x = 0} = K \sqrt{\frac{i\omega}{k}}\, T_o \tag{9}$$

This flux density must equal the power W given by Equation 5. Therefore, the temperature amplitude at the surface is

$$T_o = \frac{(1-R)\, I_o\, (1 - e^{-\alpha d})}{2K \left| \sqrt{\frac{i\omega}{k}} \right|} = \frac{(1-R)\, I_o\, (1 - e^{-\alpha d})}{2 \sqrt{\omega\, K\, C}} \tag{10}$$

c. Unmodulated-Radiation Method

In the case of an unchopped incident beam the surface temperature is controlled by the thermal spreading resistance r_1 into the concrete wall. This quantity is given by

$$r_1 = \frac{1}{\pi\, a\, K} \text{ (deg/watt)} \tag{11}$$

where a is the radius of the incident beam and K, as before, is the thermal conductivity of the concrete wall.

In addition there is another resistance due to thermal radiation from the heated surface. This effect can be represented by a thermal resistance r_2 given by

$$r_2 = \frac{1}{4\, \varepsilon\, \sigma\, T^3\, \pi\, a^2} \tag{12}$$

where ε is the thermal emittance of the wall and σ is the Stefan Boltzmann constant.

Let P be the power delivered to the absorbing layer by the incident beam. Then the temperature rise T is given by "Ohm's Law" for heat

$$T = (1-R)\ rP = \frac{(1-R)\ (1-e^{-\alpha d})\ I_o}{\frac{K}{a} + 4\ \varepsilon\sigma\ T^3} \qquad (13)$$

$$\text{where } \frac{1}{r} = \frac{1}{r_1} + \frac{1}{r_2} \qquad (14)$$

The sample calculations below show that the unmodulated-beam method is greatly be to preferred. Equation (13) applies to the case of a non-scanning beam. The temperature rise will decrease with increasing scan rate. In actual practice, a number of implementations of the precise methodology are possible. One would be to irradiate a relatively large patch of the wall and view it at the same time. The entire area could be surveyed by moving the irradiated patch and thermal viewer together. Another possibility would be to irradiate only a small moving spot (more radiation per unit area) and view a large patch over the time period necessary to irradiate the whole patch. A third possibility is to view only the irradiated small spot and move the viewer with the subject spot. The precise implementation of the scheme will depend on a number of engineering tradeoffs concerning the expected signal strength, time available to survey the area in question, and so forth.

d. Sample Calculations. Based on the formulas derived above, the AC and steady-state temperature changes were calculated using ultraviolet irradiation and thermal viewing on concrete and wood. The parameters of the calculation are given together with their sources in Table III-4. The absorption coefficient used in this calcuation was for PETN at a wavelength near 2,000 angstroms. This wavelength is shorter than the UV irradiation source peak used for calculation and some effort would have to be made to match the two. The PETN data were obtained from the Journal of Physical Chemistry, 77 910, (1973) showing a value of the absorption coefficient of 5.6×10^4 cm^{-1} between approximately 45,000 and 55,000 cm^{-1} (near 2000A). TNT in the UV region (near 2325A) has an absorption coefficient similar to that of PETN. Most of the other parameters are somewhat variable depending on the source, as the materials (concrete and wood) are variable in composition. A spectrum of TNT was run in the infrared which shows a maximum absorption coefficient of about 7,000 cm^{-1} between 6.2 and 6.7 μm. These data, which are expected to be typical of most of the compounds in the two regions, are the reason for our choice of the ultraviolet region for surface irradiation.

TABLE III-4. PARAMETERS USED IN SAMPLE CALCULATIONS

Parameter	Value	Source and Comments
R_{uv}	0.1	Estimate from the Infrared Handbook
$\bar{\alpha}_{PETN}$	5.6×10^{4} cm^{-1}	J. Phys Chem, 77, 910 (1973)
α_{TNT} (peak)	1.38×10^{5} cm^{-1}	ARLCD-TR-78025 (1978)
d	0.56×10^{-7} cm	Taken from 1 $\mu g/cm^2$, ρ_{PETN} = 1.77
I_o	5×10^{-3} watts/cm^2*	Estimate by P. von Thuna, ADL
$K_{concrete}$	8×10^{-3} watts/cm deg C	AIP Handbook
K_{wood}	2×10^{-3} watts/cm deg C	AIP Handbook
$C_{concrete}$	0.65 j/gm deg C	Marks Standard Handbook for Mechanical Engineers
C_{wood}	1.75 j/gm deg C	Handbook of Chem & Physics
$\rho_{concrete}$	1.6 g/cm^3	AIP Handbook
ρ_{wood}	0.6 g/cm^3	API Handbook
a	1 cm	-----
ω	6.28 Hz	For 1 Hz chopping frequency
ε_{IR}	0.9	Estimate from related materials
T	300°K	-----

σ, the Stefan Boltzmann Constant = 5.67×10^{-12} $\left(\frac{watts}{cm^2 deg^4}\right)$

*This value will depend on the precise wavelength, bandwidth, and geometry of UV optics.

Using formula (10) for modulated UV irradiation (PETN)

$$T_o = \frac{(1-R)\ (1 - e^{-\alpha d})\ I_o}{2\sqrt{KCP\omega}} = 0.006°C \text{ (concrete)} \quad = 0.01°C \text{ (wood)}$$

Using formula (13) for unmodulated UV irradiation (PETN)

$$\Delta T = \frac{(1-R)\ (1 - e^{-\alpha d})\ I_o}{\frac{K}{a} + 4\varepsilon\sigma\ T^3} = 0.3°C \text{ (concrete)} \quad = 1.1°C \text{ (wood)}$$

The values for TNT would be approximately the same as those for PETN as the listed value is at the peak of the absorption band which extends out to near 2800A°. The fact that the latter value are well within the measurement capabilities of commercially available thermal imaging equipment forms the basis for our conclusion that the method is technically feasible.

3. Analyte UV Absorption Characteristics

UV absorption data for the analyte PETN were presented in the preceding discussion. Data on each of the other analytes of interest was also assembled and is in Table III-5.

It should be noted that most of the data in Table III-5 are for solutions of the analytes since these properties are customarily measured and reported in that manner. It is not clear that solution data are reliable indicators of the strength or location of UV absorption bands of the solid samples because these characteristics are often strongly influenced by the solvent. However, laboratory comparison of UV absorption spectra of the analyte 2,4-DNP in acetonitrile solution and in a KBr pellet and showed that the wavelengths corresponding to maximum absorption and the calculated absorption coefficients are quite similar. To the extent that this is also the case for the other analytes (and depending on the solvents), the data in Table III-5 may, in fact, indicate that relative locations and strengths of UV absorption bands. In that case, the data in Table III-5 suggest the following:

1. With the exception of NG, all analytes exhibit comparable absorption strengths (i.e., ε and α in Table III-5 are on the same order of magnitude for all analytes). Thus, the proposed approach should be equally applicable to all analytes;

2. The absorption bands of all analytes are sufficiently close to 2500 Angstroms that an illumination source capable of providing sufficient power output over some wavelength range centered on or about this wavelength may permit detection of all analytes (except NG). Commercially available mercury sources which emit the characteristic 2537 Angstrom line may be suitable for this purpose.

TABLE III-5. UV ABSORPTION DATA FOR ANALYTES IN SOLUTION

Compound	Solvent	λ(Å)	ε(L/mole cm)	α(cm^{-1})	Reference
TNT	Ethanol	2270	19,500		1
	H_2O	2320	19,000	1.38×10^5	4
2,4 Dinitrotoluene	C_5H_{12}	2320	15,850	1.32×10^5	1
	Ethanol	2405	14,125		
2,6 Dinitrotoluene	C_5H_{14}	2270	12,000	8.48×10^4	1
RDX	Methanol	2360	10,000		1
	Solid	2360	11,000	9.02×10^4	3
	H_2O	2400	10,000		1
	Ethanol	2130	11,000		1
PETN	Acetonitrile	2000	10,000	5.6×10^4	8
		2220 (not peak)	~2,000	~1.1×10^4	
Nitroglycerine	H_2O	2760	10	70	7
Tetryl	Ethanol	2250	25,100	1.37×10^5	1
Diphenylamine	Methanol or Ethanol	2850	20,400	1.4×10^5	1
	Ethanol, 77°K	5500	31,000	2.12×10^5	5
1,3,5 Trinitrobenzene	50-50, Methanol-H_2O	2250	25,700	2×10^5	6
	C_7H_{16}	2800	550		1
	C_7H_{16}	3500	182		1
	C_7H_{16}	2220	31,600		1
	Ethanol	2250	25,700		1
2,4 Dinitrophenol	H_2O	3600	17,800	1.63×10^5	2
	Ethanol	2920	9,100		1
	Ethanol	2530	10,200		1

ε = molar absorptivity; α = εc

Table II-5 (Continued

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UV Absorption data for solutions of analytes were presented in Table III-6. We also obtained solid state UV absorption coefficients of six analytes to determine whether the tentative conclusions based on examination of solution data could be confirmed. A technique used extensively in infrared analysis--the preparation of KBr pellets containing the analyte--was attempted and found to be satisfactory through the Cary 219, 400-200nm, ultraviolet range. Macropellets of 13-mm diameter were pressed under 20,000 pounds pressure, using oven-dried KBr to prevent moisture from clouding the pellet.

Initial attempts to use a Wig-L-Bug device to thoroughly mix sample and KBr proved unsatisfactory--inexplicable clouding occurred, even in thoroughly dried containers. A successful method finally used involved gentle but thorough grinding in a mortar and pestle. Some experimentation was necessary to determine the right concentration to yield a measurable peak.

Two methods of measurement were used, both giving comparable results. The first method involved plotting an air vs. air baseline, then obtaining both blank KBr pellet and sample KBr pellet traces. At the sample peak, the blank reading was subtracted. In the second method, a baseline was obtained with blank KBr pellets in each beam. When the sample pellet was substituted on the sample side, the absorbance at the peak could be read directly.

Thickness of the pellets was measured with a micrometer and calculations made as noted in Table III-6. These findings confirm the tentative conclusions noted earlier.

4. Laboratory Demonstration.

The thermal imaging equipment required for laboratory demonstration of the practical utility of the UV illumination/thermal imaging sampling protocol was rented from Inframetrics, Inc. for one week. Using this equipment and UV illumination sources already on hand in Arthur D. Little, Inc. laboratories, we were able to observe the presence of small quantities of solid analyte on all of the available surface types of interest except brick. However, the observed contrast between analyte and surrounding surfaces was less than would be desirable for routine field use. Independent measurements indicated that the power output of the UV illumination sources used was on the order of 150 microwatts to 1 milliwatt, which is less than that assumed in calculations above. Substitutions of the experimental values for UV power output in those calculations results in a predicted temperature rise on the order of that which was, in fact, observed. Thus, while these experiments confirm the practical utility of the method, they also indicate that for optimum performance a UV illumination source having a higher power output in the desired wavelength region should be used. We expect that a UV source with the desired performance characteristics and operational characteristics that would permit its safe use under field conditions can be obtained commercially.

TABLE III-6. SOLID STATE ANALYTE UV ABSORPTION COEFFICIENTS

Sample	Wt. Sample mg	Density g/cc	Wt. KBr mg	Density g/cc	λ Max nm	Abs.*	Thickness mm	$\alpha(cm^{-1})$
1,3,5-TNB	.029	1.688	324.888	2.75	230	1.65(2)	.935	1.21×10^5
					228	1.70(1)	.935	1.25×10^5
2,4-DNP	.059	1.683[24]	199.74	2.75	262	2.62(1)	.60	$.90 \times 10^5$
2,4-DNT	.050	1.521[15]	320.111	2.75	264	1.52(1)	.91	$.59 \times 10^5$
RDX	.446	1.82[20]	319.654	2.75	240	.86(1)	.90	$.045 \times 10^5$
					240	.86(2)	.90	$.045 \times 10^5$
2,4,6-TNT	.136	1.654	260.114	2.75	240	.54(2)	.73	$.085 \times 10^5$
Tetryl	.127	1.57[19]	250.179	2.75	228	.38(2)	.69	$.062 \times 10^5$

*Correction made for KBr absorbance by subtraction or using dual beam method with blank KBr in reference side.

(1) Subtraction method.

(2) Dual beam method.

$$\alpha(cm^{-1}) = \frac{\text{Absorbance}}{\frac{cm^3 \text{ Sample}}{cm^3 \text{ KBr}} \times \text{macropellet thickness in cm}}$$

E. ANALYTE DETECTION USING UV IRRADIATION AND UV PHOTOGRAPHY:

1. Background.

UV light directed at analytes present on a surface may be 1) transmitted, 2) reflected, or 3) absorbed. Measurement of the temperature rise resulting from UV absorption is the principle underlying the thermal imaging approach. Any UV absorption will necessarily be accompanied by a decrease in the UV reflectance, and observation of the latter quantity may also be a feasible detection method. In this case, surfaces on which analytes are present would appear as dark areas against a lighter background when illuminated with a UV source and viewed with a UV selective detector. The detector could consist simply of black and white film in a large format camera equipped with a UV filter centered on or about 2500 Angstroms. The advantages of this approach would include the simplicity and ease of operation of the required equipment and the fact that the resulting photographs could be maintained as a permanent record of the investigations.

2. Preliminary Experiments.

Two types of experiments were performed to assess the practical utility of this approach. In one experiment, the diffuse UV reflectance from a concrete surface to which 60 $\mu g/cm^2$ of 2,4-DNP were added was measured in a UV spectrophotometer. About a 59% reduction in reflectance at 3600 Angstroms was observed. This observation suggested that for concrete and probably for other surface types as well, the anticipated effects were, in fact, observed and that the measurements could probably also be made at much lower analyte concentrations.

In a second set of experiments, UV photographs of several analytes spiked on surfaces were obtained. Figure III-7 is a photograph showing the contrast obtained for 2,4-dinitrophenol, tetryl, 2,6-dinitrotoluene, RDX and TNT in 1.3×10^{-4} g/cm^2 amounts on a thin layer chromatography silica gel substrate. The photograph was obtained using a 2400 A filter and a Ziess HBO 200 W source with the glass lens removed.

Figure III-8 shows the concentration sensitivity for differing amounts TNT, tetryl and 2,4-dinitrophenol on concrete using a 3650 A filter. The top row has concentrations of approximately 6×10^{-5} g/cm^2 for each material (including the amount lost by diffusion into the substrate). The second row has about twice the amount of TNT and half the amounts of tetryl and 2,4-dinitrophenol although the spot size is somewhat variable.

Characteristics of the UV irradiation and viewing filter would have to be optimized for maximum contrast. Additional experiments using different UV illumination sources and narrow bands pass UV filters were performed to establish the optimum conditions for UV photography.

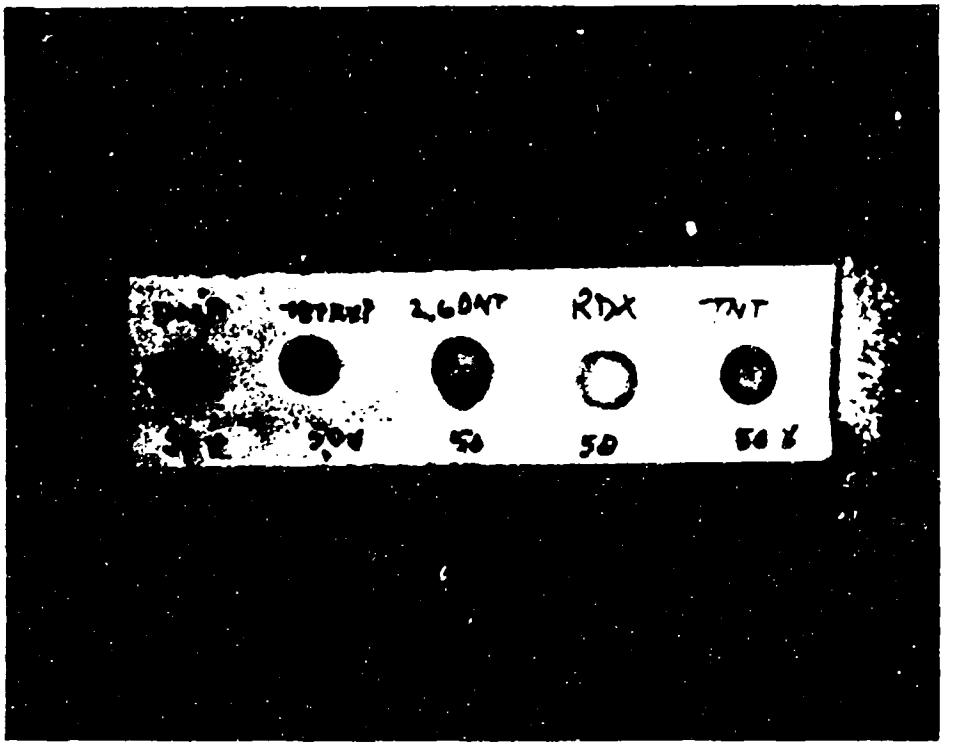

Figure III-7. UV Photography of 130 $\mu g/cm^2$ Each of 2,4-DNT, Tetryl, 2,6-DNT, RDX, and TNT on TLC Plate

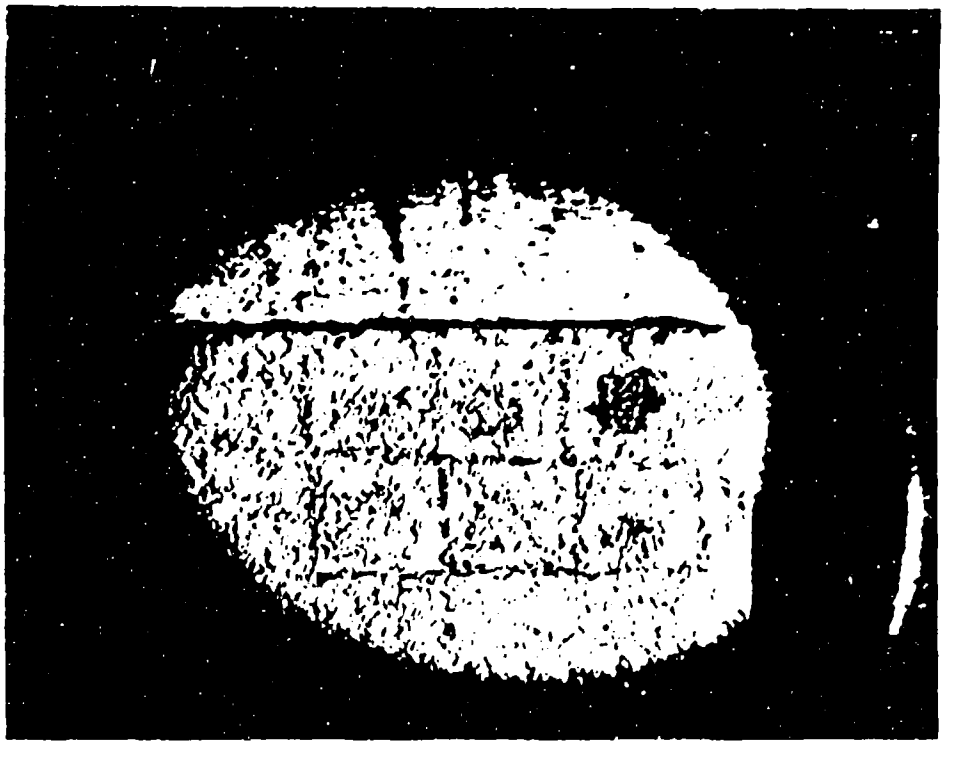

Figure III-8. UV Photography of TNT, Tetryl, and 2,4-DNP on Concrete

The camera and lens for these experiments consisted of long bellows Bausch and Lomb microscope camera that could be converted to a horizontal position. The camera has a variable shutter to which we could attach a simple, 250 mm focal length, quartz lens. A variable iris was used to reduce the aperture and thus effectively increase the depth of field. This procedure compensated for the change in effective focal length encountered when focussing with visible light then photographing at a shorter wavelength, thus throwing the image out of focus.

This camera has a 4 x 5 sheet film format with which we used Polaroid P/N 55 sheet film providing both the positive print and a negative. The film is a slow high resolution type film with apparent adequate sensitivity to the ultraviolet to allow a relatively short exposure time. Five seconds was adequate with the Zeiss lamp.

The experiments described previously utilized a high pressure mercury arc (Zeiss HBO 200 Watt) which produces a substantial amount of energy centered on the 365 nm mercury emission line. This radiation was selectively transmitted to the camera lens with the use of a barrier filter with a maximum transmission at 365 nm.

In additional experiments, a Mineralite Model S-61 source was obtained for evaluation. This is a low pressure mercury lamp which is reported to have a higher intensity of 254 nm radiation. This lamp is of particular interest as a radiation source for the thermal imaging experiments where it is essential to optimize the absorption of radiation to achieve the maximum subsequent thermal emission. With this lamp as a light source, a series of photographs were taken of the test spots of explosives on various substrates using different barrier filters. Experimentally it was determined that a 10-minute exposure was required to produce an adequate image using a 254 nm band pass barrier filter over the camera lens.

The results of these experiments are shown in Table III-7.

These data indicate that it takes a much longer exposure interval to obtain a suitable image with the shorter 254 nm radiation. This would not be a significant handicap if there were a distinct advantage to be gained. However, we observe approximately the same level of gray image for each of the representative substrates for both radiation sources. In order to successfully photograph any explosive residue, it is obvious that the image must appear darker than the background or substrate material. In our evaluation we have applied the explosive compound to silica thin layer chromatography substrates as a standard of comparison. A good contrast image was obtained for most of the explosives on this substrate and 50 microgram spots could be detected for most of the compounds. Nitroglycerine and PETN did not absorb at this wavelength and do not photograph well under these conditions.

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[1] Ultraviolet Products, Inc., South Pasadena, CA

TABLE III-7. RESULTS OF UV PHOTOGRAPHIC EXPERIMENTS

Radiation Source	High Pressure Hg Arc Hg Arc, Zeiss	Low Pressure Hg Arc, Mineralite
Most intense UV radiation	365 nM	254 nM
Optimum barrier filter for camera	365 nM	254 nM
Exposure level (film response)	5 seconds	10 minutes
Substrate Response:		
Silica, Chromatograph plate	White	White
Concrete block	Light gray	Light gray
Transite	Medium gray	Medium gray
Galvanized steel	Reflective	Reflective
Brick	Dark gray	Dark gray
Wood	Dark gray	Dark gray
Glass		Black

Typical examples of these results are shown in attached photographs. These photographs were taken using the low pressure mercury source with an exposure of 10 minutes. Figure III-9 was taken with the 365 nm transmission filter over the lens. We note excellent contrast for DNP, tetryl and TNT. Figure III-10 shows the effect of using the 254 nm tansmission filter which changes the focal length with the shorter wavelength. It is interesting to note that the DNP and tetryl have less contrast at this shorter wavelength, while RDX has slightly better contrast.

Figure III-10 includes a sample of transite containing 50 micrograms quantities of applied explosives. Recognizable spots are noted for DNP, tetryl, RDX and TNT while TNB is barely visible.

It has been reported that normal optical glass will transmit enough 365 nm radiation that suitable photographs can be produced with a conventional camera lens. However, this would be a less than optimum condition and totally ineffective for the 254 nm radiation and therefore not investigated.

Taken together, these results suggest that further investigation of this approach appears to be warranted. In particular, it would be desirable to evaluate under actual field conditions the ability of this approach to detect those analytes for which these experiments indicate it is best suited.

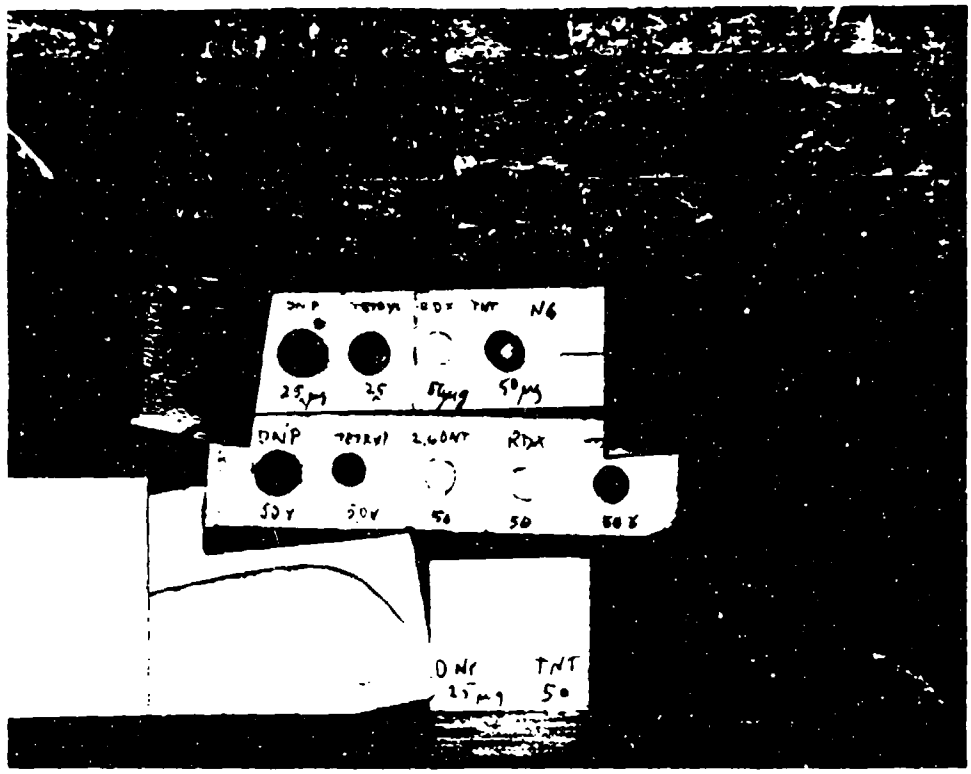

Figure III-9. Analytes on Silica Gel and Metal. 365 nm

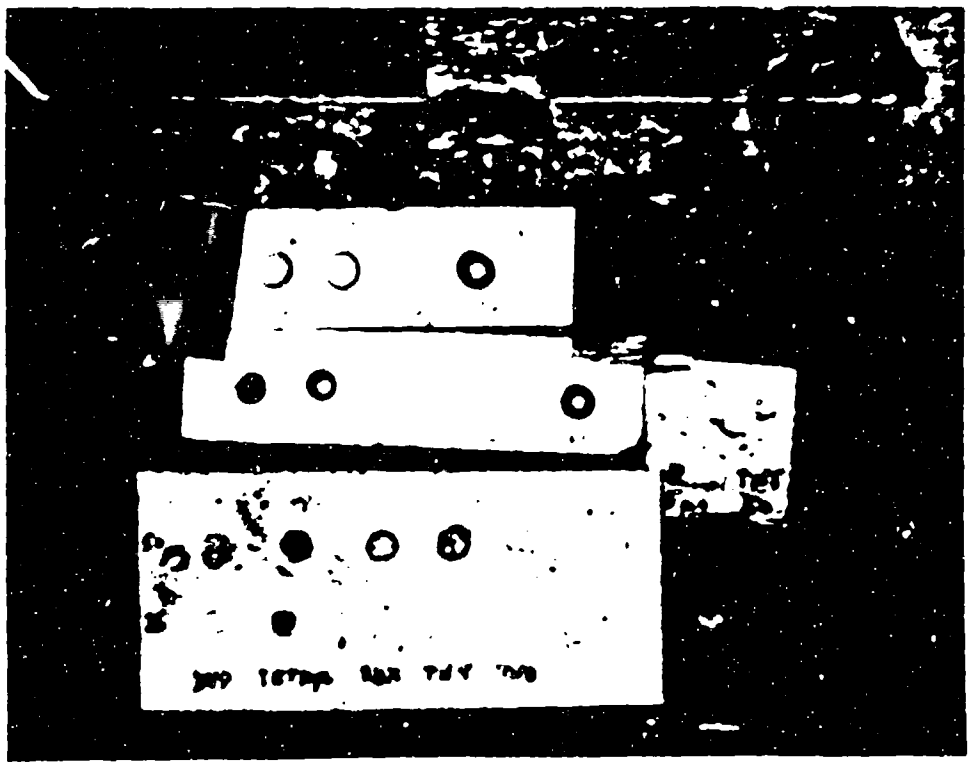

Figure III-10. Analytes on Silica Gel (top) and Transite (bottom). 254 nm

IV. QUANTITATIVE METHODS DEVELOPMENT

A. INTRODUCTION

The quantitative method selected for developmental testing involved solvent extraction using alternative procedures to conventional wipe or swab methods. Existing USATHAMA methods for the determination of explosives, modified as necessary for this particular application, were used for analysis of the resulting extract.

The objective of this testing was development of procedures for quantitative determination of specific compounds down to concentrations as low as 5 μg/10 cm^2. The approach used to achieve this objective involved in each case the spiking with known amounts of analytes of new, uncontaminated samples of each of the surface types of interest obtained from building materials dealers. The samples of conductive non-sparking flooring that were available for this study were known to have been contaminated with explosives/explosive residues, thereby precluding the spike and recovery approach. The results obtained by applying the procedures developed for other surface types to samples of this material are described in Section IV.C.3.

At the direction of the Technical Project Officer, emphasis was placed on the development of procedures for organic analytes. Methods based on an extraction approach similar to that described in this report for organic compounds are used widely for the determination of inorganic species, including those of interest in this study, in soils, sediments, sludges, etc. No methods for inorganic species which would represent substantive improvement over those methods were finally identified.

B. SEMIQUANTITATIVE CERTIFICATION TESTING

Preliminary semiquantitative certification was accomplished by spking analytes into the quantity of acetonitrile specified in the existing USATHAMA method prior to any concentration or solvent exchange steps, and continuing through the steps of the analytical method. The certification test involved analyzing five analyte concentrations plus a blank, one time each on three or more days. The resulting data is summarized in Volume II of this report.

Tables IV-1 and IV-2 summarize the analytical method conditions and the statistical data, respectively. (Tables IV-1 and IV-2 are reproduced as Tables I-1 and I-2 in Volume II of this report).

C. QUANTITATIVE CERTIFICATION TESTING

1. Introduction

Quantitative certification was accomplished as noted above by spiking analytes in acetonitrile solution directly onto new, uncontaminated samples of each of the surface types of interest, extracting the spiked

ANALYTICAL METHOD CONDITIONS

Analyte	Instrument	Column	Precolumn	Program Temp or Solvent	Retention Time	Solvent System/ Carrier Gas	Flow Rate
PETN	HPLC	Spherisorb ODS, 5μ, 250 x 4.6 mm	Pellicular LC-18, 40μ, 50 x 4.6 mm	Isocratic	6.2 min	65/35 CH_3CN/H_2O	1 ml./min
2,6-DNT	HPLC	Spherisorb ODS, 5μ, 250 x 4.6 mm	Pellicular LC-18, 40μ, 50 x 4.6 mm	Isocratic	24.6 min	35/65 CH_3CN/ .005M t-butyl	1 ml./min
NG	HPLC	Spherisorb ODS, 5μ, 250 x 4.6 mm	Pellicular LC-18 40μ 50 x 4.6 mm	Isocratic	30.5 min	ammonium hydroxide	1 ml./min
2,4-DNT	GC	3% OV-225 on 100/120 Gas ChromQ ¼" x 2 mm ID x 6' glass column	None	100C for 6 min 15C/min to 165C;	19.90 min	5% Methane/argon	30 ml./min
2,6-DNT	GC	3% OV-225 on 100/120 Gas ChromQ ¼" x 2 mm ID x 6' glass column	None	hold 8 min 15C/min to 200 C;	16.20 min	5% Methane/argon	30 ml./min
1,3,5-TNB	GC	3% OV-225 on 100/120 Gas ChromQ ¼" x 2 mm ID x 6' glass column	None	hold 6 min	30.95 min	5% Methane/argon	30 ml./min
2,4,6-TNT	GC	3% OV-225 on 100/120 Gas ChromQ ¼" x 2 mm ID x 6" glass column	None	"	28.14 min	5% Methane/argon	30 ml./min
DPA	HPLC	U Bondpack C18 4mm x 30 cm	None	Isocratic	230 sec	90/10 methanol/H_2O	1 ml./min
Tetryl	HPLC	U Bondpack C18 4mm x 30 cm	None	Isocratic	416 sec	60/40 methanol/H_2O	1 ml./min
DNP	HPLC	Spherisorb ODS, 5μ, 250 x 4.6 mm	Pellicular LC-18,40μ 50 x 4.6 mm	Initial: 30% CH_3CN Final: 50% CH_3CN Time: 35 min Gradient: linear	12.5 min	0.08M acetic acid adjusted to pH 3.1 with ammonium hydroxide/CH_3CN	1.0 ml./min
RDX	HPLC	Spherisorb ODS, 5μ, 250 x 4.6 mm	Pellicular LC-18, 40μ 50 x 4.6 mm	Initial: 30% CH_3CN Final: 50% CH_3CN Time: 35 min Gradient: linear	13.5 min	0.08M acetic acid adjusted to pH 3.1 with ammonium hydroxide/CH_3CN	1.0 ml./min
TNB	HPLC	Spherisorb ODS, 5μ, 250 x 4.6 mm	Pellicular LC-18,40μ 50 x 4.6 mm	Initial: 30% CH_3CN Final: 50% CH_3CN Time: 35 min Gradient: linear	17.2 min	0.08M acetic acid adjusted to pH 3.1 with ammonium hydroxide/CH_3CN	1.0 ml./min
2,4-DNT	HPLC	Spherisorb ODS, 5μ, 250 x 4.6 mm	Pellicular LC-18, 40μ 50 x 4.6 mm	Initial: 30% CH_3CN Final: 50% CH_3CN Time: 35 min Gradient: linear	24.3 min	0.08M acetic acid adjusted to pH 3.1 with ammonium hydroxide/CH_3CN	1.0 ml./min
TNT	HPLC	Spherisorb ODS, 5μ, 250 x 4.6 mm	Pellicular LC-18, 40μ 50 x 4.6 mm	Initial: 30% CH_3CN Final: 50% CH_3CN Time: 35 min Gradient: linear	25.6 min	0.08M acetic acid adjusted to pH 3.1 with ammonium hydroxide/CH_3CN	1.0 ml./min
Tetryl	HPLC	Spherisorb ODS, 5μ, 250 x 4.6 mm	Pellicular LC-18, 40μ 50 x 4.6 mm	Initial: 30% CH_3CN Final: 50% CH_3CN Time: 35 min Gradient: linear	26.7 min	0.08M acetic acid adjusted to pH 3.1 with ammonium hydroxide/CH_3CN	1.0 ml./min
DPA	HPLC	Spherisorb ODS, 5μ, 250 x 4.6 mm	Pellicular LC-18,40μ 50 x 4.6 mm	Initial: 30% CH_3CN Final: 50% CH_3CN Time: 35 min Gradient: linear	39.2 min	0.08M acetic acid adjusted to pH 3.1 with ammonium hydroxide/CH_3CN	1.0 ml./min

TABLE IV-2. SEMIQUANTITATIVE CERTIFICATION TESTING
STATISTICAL DATA SUMMARY

Analyte	Detector	Atten.	Chart Speed	Inj. Volume	USATHAMA Method	Det. Limit	Corr. Coeff.	Slope	Int.	MPR Reference
PETN	UV at 230 nm	0.01 AUFS	0.1 in/min	70 uL	none	1.77 ug/mL	0.996	1.046	0.450	9
2,6-DNT	UV at 230 nm	0.01 AUFS	0.1 in/min	70 uL	MRI Method	0.26 ug/mL	0.998	1.061	9.888	8
NG	UV at 230 nm	0.01 AUFS	0.1 in/min	70 uL	MRI Method	4.54 ug/mL	0.999	0.989	2119.5	8
2,4-DNT	ECD @300C	$1x10^{-11}$x8	0.5 cm/min	1 uL	246 TNT-WA-02	0.11 ug/mL	0.967	0.743	0.034	5
2,6-DNT	ECD @300C	$1x10^{-11}$x8	0.5 cm/min	1 uL	246 TNT-WA-02	0.09 ug/mL	0.989	1.069	-0.012	5
1,3,5-TNB	ECD @300C	$1x10^{-11}$x8	0.5 cm/min	1 uL	246 TNT-WA-02	0.12 ug/mL	0.999	1.058	0.007	5
2,4,6-TNT	ECD @300C	$1x10^{-11}$x8	0.5 cm/min	1 uL	246 TNT-WA-02	0.12 ug/mL	0.979	1.054	-0.009	5
DPA	UV at 254 nm	0.1 AUFS	0.5 cm/min	200 uL	DPA-WA-01	12.25 ug/mL	0.997	0.796	-0.634	3
Tetryl	UV at 254 nm	0.1 AUFS	0.5 cm/min	200 uL	TETRYL-WA-02	0.08 ug/mL	0.995	0.862	-0.004	5
DNP	UV at 254 nm	0.01 AUFS	0.1 in/min	100 uL	MRI Method	30 ng/mL	0.998	0.971	5.397	10
RDX	UV at 254 nm	0.01 AUFS	0.1 in/min	100 uL	MRI Method	70 ng/mL	0.998	1.009	9.698	10
TNB	UV at 254 nm	0.01 AUFS	0.1 in/min	100 uL	MRI Method	25 ng/mL	0.999	0.994	0.674	10
2,4-DNT	UV at 254 nm	0.01 AUFS	0.1 in/min	100 uL	MRI Method	24 ng/mL	0.999	0.990	1.585	10
TNT	UV at 254 nm	0.01 AUFS	0.1 in/min	100 uL	MRI Method	24 ng/mL	0.999	1.012	0.269	10
Tetryl	UV at 254 nm	0.01 AUFS	0.1 in/min	100 uL	MRI Method	25 ng/mL	0.999	1.050	-5.410	10
DPA	UV at 254 nm	0.01 AUFS	0.1 in/min	100 uL	MRI Method	51 ng/mL	0.999	0.993	7.745	10

samples with acetonitrile using ultrasonic agitation, and analytical procedures used for preliminary certification. The analytical methods that we developed were evaluated according to the procedures specified in the 1980 USATHAMA QA Plan. The resulting data is summarized in Volume II of this report.

2. Analytical Methods

The analytical procedures that were developed and evaluated are described in detail on pages 76 through 87 of Volume I of this report. (These analytical methods are also presented on pages 46 through 57 of Volume II of this report.

3. Results and Discussion

Table IV-3 summarizes the statistical data obtained from Quantitative Certification Testing. (Table IV-3 is reproduced as Table II-1 in Volume II.)

As noted above (Section IV.A), the samples of conductive non-sparking flooring that were available for this study were known to have been contaminated with explosives/explosive residues, thereby precluding quantitative certification testing. Instead, the analytes of interest were determined in these samples by the methods described in Section III.C.2.

Two samples of conductive non-sparking flooring from an operating explosives building were received from Dr. Harold J. Matsuguma, Chief, Chemistry Branch, Energetic Materials Division, ARADCOM. One sample consisted of a single large sheet about two square feet in area which reportedly represents a commonly used roll material. The other sample consisted of several small chunks which reportedly represent another conductive coating which is trowelled onto a floor and allowed to harden.

Of the analytes of interest in this study, these samples were reportedly exposed to RDX, TNB, TNT, tetryl, and PETN. Two subsamples, each approximately 10 cm^2 in area, of each of the two flooring types were extracted with acetonitrile using ultrasonic agitation and the analytes RDX, TNB, TNT, and tetryl were determined in the resulting extracts. The results of these analyses are presented in Table IV-4.

Analysis of wood samples spiked with explosives using these analytical methods met with mixed results. For many samples, analyte detection limits and recoveries comparable to those obtained for other analyte-surface combinations were obtained. However, in certain samples large interfering peaks which precluded identification and quantification of the analytes of interest were observed. These interferences appeared unpredictably among subsamples taken from a single piece of kiln-dried dimension lumber obtained from a local building materials dealer, and are presumed to be due to naturally-occurring compounds distributed

TABLE IV-3. QUANTITATIVE CERTIFICATION TESTING STATISTICAL DATA SUMMARY

	Metal		Concrete		Brick		Transite	
	D.L. $\mu g/cm^2$	% Rec	D.L. $\mu g/cm^2$	% Rec	D.L. $\mu g/cm^2$	% Rec	D.L. $\mu g/cm^2$	% Rec
DNP	0.33	96%	1.74 (0.35	31% 34%)[2]	1.59	55%	2.22 (1.15	34% 30%)[2]
RDX	0.25	96%	0.63	78%	2.11	72%	3.48 (0.80	67% 82%)[2]
TNB	0.28	95%	0.98	75%	2.12	74%	3.46 (0.76	59% 71%)[2]
2,4-DNT	0.90	84%	1.08	78%	2.10	69%	3.52 (0.62	65% 79%)[2]
2,4,6-TNT	0.60	97%	1.57	74%	1.68	66%	3.18 (0.68	51% 60%)[2]
Tetryl	1.95	88%	4.29	51%	2.60	68%	4.13	56%
DPA	0.50	94%	2.44 (1.15	74% 84%)[2]	2.14	69%	3.71 (0.90	67% 82%)[2]
2,6-DNT	2.85	94%	6.46	86%	6.36	49%	2.04	79%
NG	9.36	94%	21.7	76%	32.5	44%	26.1	72%
PETN	10.2	86%	5.39	83%	20.6	62%	10.0	82%

[1] Calculated from four days of target vs. found concentrations using the procedures specified in the 1980 USATHAMA QA Plan.

[2] Calculated from three days of target vs. found concentrations.

QUANTITATIVE METHOD FOR THE DETERMINATION OF DNP, RDX, TNB, 2,4-DNT, TNT, TETRYL, AND DPA ON SURFACES

1. Application

Method used to extract the following compounds from metal, brick, concrete, transite surfaces:

2,4,6-dinitrophenol DNP
cyclotrimethylenetrinitramine RDX
1,3,5-trinitrobenzene TNB
2,4-dinitrotoluene 2,4-DNT
2,4,6-trinitrotoluene 2,4,6-TNT
2,4,6-trinitrophenylmethylnitramine Tetryl
diphenylamine DPA

A. Tested Concentration Range

DNP	0.25 $\mu g/cm^2$	- 5.00 $\mu g/cm^2$
RDX	0.25 $\mu g/cm^2$	- 5.00 $\mu g/cm^2$
TNB	0.25 $\mu g/cm^2$	- 5.00 $\mu g/cm^2$
2,4-DNT	0.25 $\mu g/cm^2$	- 5.00 $\mu g/cm^2$
TNT	0.25 $\mu g/cm^2$	- 5.00 $\mu g/cm^2$
Tetryl	0.25 $\mu g/cm^2$	- 5.00 $\mu g/cm^2$
DPA	0.25 $\mu g/cm^2$	- 5.00 $\mu g/cm^2$

B. Sensitivity

Instrument response for each analyte is given below:

Analyte	Concentration	Response
DNP	25.04 ng/mL	3700 area units
RDX	24.86 ng/mL	1388 area units
TNB	24.97 ng/mL	4437 area units
2,4-DNT	24.99 ng/mL	6090 area units
TNT	24.91 ng/mL	4104 area units
Tetryl	25.30 ng/mL	2895 area units
DPA	24.91 ng/mL	2101 area units

C. Detection Limit

See Table II-1.

D. Interferences

Interferences present in some brick and transite samples were apparently random rather than systematic. For example, the HPLC analysis of extraction B of one blank (unspiked) brick surface (extracted for 4)

indicated the presence of a compound with a retention time of 1510 seconds. This compound interfered with the TNT. However, this interference was not observed in any other blank brick sample. Therefore, only the brick samples analyzed on Feb 9 were corrected for the interference.

E. Analysis Rate

Six samples can be extracted and prepared for analysis in three hours. Rate of analysis is given below, excluding calibration standards:

DNP	8 samples in an 8 hour day
RDX	8 samples in an 8 hour day
TNB	8 samples in an 8 hour day
2,4-DNT	8 samples in an 8 hour day
TNT	8 samples in an 8 hour day
Tetryl	8 samples in an 8 hour day
DPA	8 samples in an 8 hour day

2. Chemistry

2,4,-dinitrophenol C6H4N2O5
CAS RN 51-28-5
MP 112-114C

Cyclotrimethylenetrinitramine C3H6N6O6
CAS RN 121-82-4
MP 205-206C

1,3,5-trinitrobenzene C6H3N3O6
CAS RN 99-35-4
MP 122.5C

2,4-dinitrotoluene C7H6N2O4
CAS RN 121-14-2
MP 71C

2,4,6-trinitrotoluene C7H5N3O6
CAS RN 118-96-7
MP 80.1C

2,4,6-trinitrophenylmethylnitramine
CAS RN 479-45-8
MP 130C Explodes 187C

diphenylamine C12H11N
CAS RN 122-39-4
MP 53-54C BP 302C

3. Apparatus

A. Instrumentation

Waters Associates Model 6000A Solvent Delivery System
Waters Associates Model M-45 Solvent Delivery System
Waters Associates Model 660 Solvent Programmer
Waters Associates Model 440 Absorbance Detector
Waters Associates Intelligent Sample Processor (WISP)
Spectra-Physics Minigrator
Hewlett Packard 7133A Recorder

B. Parameters

Column: Spherisorb ODS 5μ, 250 x 4.6 mm ID
Precolumn: Pellicular LC-18, 40μ, 50 x 4.6 mm ID
Solvent System: linear gradient
  Initial: 30/70 CH_3CN/0.08 M acetic acid adjusted to pH 3.1 with NH_4OH
  Final: 50/50 CH_3CN/0.08 M acetic acid adjusted to pH 3.1 with NH_4OH
  Time: 35 minutes
Detector: UV at 254 nm
Flow Rate: 1.0 mL/min
Attenuation: 0.01 AUFS
Injection Volume: 100 μL

C. Hardware/Glassware

Westinghouse Ultrasonic cleaner
8 ounce jars with teflon lined caps
25 mL graduated cylinders
microliter syringes
volumetric flasks - 50, 10, 5 mL
vials - WISP and 14 mL, with teflon lined caps

D. Chemicals

acetonitrile, HPLC grade
nitrogen
acetic acid
ammonium hydroxide
Standard Analytical Reference Material for each analyte

4. Standards

A. Calibration Standard

Stock Solution A: DNP, RDX, TNB, 2,4-DNT, TNT, TETRYL, DPA
Prepare individual stock solutions of 5.0 mg/mL. Combine 500 µL individual stocks and dilute to 5 mL.

Stock Solution B:
Dilute 625 µL Stock Solution A to 5 mL. Concentration is 62.5 µg/mL of each analyte

Calibration standards prepared in 25 mL volumetrics adding H_2O so final solution is 55% H_2O/45% CH_3CN:

Cal Std.	µL Stock B Added	Concentration Each Analyte
1	10	25.0 µgL
2	20	50.0 µgL
3	40	100.0 µgL
4	80	200.0 µgL
5	200	500.0 µgL
6	400	1000.0 µgL

B. Control Spikes

Spiking stock solutions were prepared using 0.5 mg/mL stock solution.

µL Stock Soln/x mL CH_3CN	Concentration Each Analyte
125 µL/10 mL	6.2 mgL
250 µL/10 mL	12.0 mgL
500 µL/10 mL	25.0 mgL
500 µL/5 mL	50.0 mgL
625 µL/5 mL	62.5 mgL
1250 µL/5 mL	125.0 mgL
2500 µL/5 mL	250.0 mgL

400 µL 6.2, 12.5, 25.0, 62.5, 125.0 mgL Stocks spiked onto 10 cm^2 concrete and metal surfaces.

200 µL 12.5, 25.0, 50.0, 125.0, 250.0 mgL stocks spiked onto 10 cm^2 brick and transite surfaces.

Concentration of analytes on surface after spiking: 2.5 µg, 5.0 µg, 10.0 µg, 25.0 µg, 50 µg.

5. Procedure

Extraction A

1. Spike 10 cm^2 surface sample with acetonitrile spike solution (volume dependent on surface type). Allow solvent to evaporate.

2. Transfer sample to 8 ounce jar and add 20 mL CH_3CN. Cover jar with teflon lined cap.

3. Sonicate for 10 minutes.

4. Transfer extract A to 50 mL volumetric flask, add 27 mL 0.08 M acetic acid and bring to volume with CH_3CN. Save surface sample for extraction B.

Extract A ready for analysis.

Extraction B

1. Add 20 mL CH_3CN to jar with surface sample. Sonicate for 10 minutes.

2. Transfer surface sample to a second jar. Add 20 mL CH_3CN and sonicate for 10 minutes more.

3. Combine extracts from steps 1 and 2 and evaporate using nitrogen to less than 5 mL.

4. Transfer evaporated extract to 10 mL volumetric flask. Add 5.5 mL to 0.08 M acetic acid and bring to volume with CH_3CN.

Extract B ready for analysis.

6. Calculations

Calculate found concentration for each analyte in each sample extract from daily calibration data.

Multiply found concentration by extract volume to find total µg in extract. Combine total µg in extracts A and B to find total µg on surface.

7. References

Lakings, D.B., Baker, R.J., and Crook, M.V., "Precision and Accuracy Assessment of the High Performance Liquid Chromatographic Analytical Technique for the Determination of Dinitrophenol (DNP); Cyclotrimethylene trinitramine (RDX); 1,3-Dinitrobenzene (DNB); 1,3,5-Trinitrobenzene (TNB); 2,4-Dinitrotoluene (2,4-DNT); Trinitrotoluene (TNT); 2,4,6-Trinitrophenylmethylnitramine (Tetryl); and Diphenylamine (DPA)", Midwest Research Institute Technical Report No. 1, USATHAMA Contract No. DAAK11-81-C-0007, March, 1981.

QUANTITATIVE METHOD FOR THE DETERMINATION OF 2,6-DNT AND NG ON SURFACES

1. Application

Method used to extract the following compounds from metal, brick, concrete, transite surfaces:

2,6-dinitrotoluene 2,6-DNT
nitroglycerine NG

A. Tested Concentration Range

2,6-DNT	1.00 $\mu g/cm^2$ to 20.00 $\mu g/cm^2$
NG	12.50 $\mu g/cm^2$ to 125.00 $\mu g/cm^2$

B. Sensitivity

Instrument response for each analyte is given below:

Analyte	Concentration	Response
2,6-DNT	0.10 µg/mL	206750 area units
NG	1.25 µg/mL	186010 area units

C. Detection Limit

See Table II-1.

D. Interferences

No interferences were observed

E. Analysis Rate

Six samples can be extracted and prepared for analysis in three hours. Rate of analysis is given below excluding calibration standards:

2,6-DNT	16 Samples in an 8 hour day
NG	16 samples in an 8 hour day

2. Chemistry

2,6-dinitrotoluene $C_7H_6N_2O_4$
CAS RN 606-20-2
MP 66C

Nitroglycerine $C_3H_5N_3O_9$
CAS RN 55-63-0
MP Stable form 13.5C

3. Apparatus

A. Instrumentation

Beckman Model 110A Solvent Metering Pump
Waters Associates Model 450 Variable Wavelength Detector
Waters Associates Model U6K Injector
Hewlett Packard 3390A Integrator/Recorder

B. Parameters

Column: Spherisorb ODS, 5μ, 250 x 4.6 mm ID
Precolumn: Pellicular LC-18, 40 μ, 50 x 4.6 mm ID
Solvent System: 35/65 CH_3CN/0.005 m t-butyl ammonium hydroxide, pH 6.5. adjusted with 1N H_3PO_4
Detector: UV at 230 nm
Flow Rate: 1.0 mL/min
Attenuation: 0.01 AUFS
Injection Volume: 100 μL

C. Hardware/Glassware

Westinghouse Ultrasonic cleaner
8 ounce jars with teflon lined caps
25 mL graduated cylinders
microliter syringes
volumetric flasks - 50, 10, 5 mL
vials - WISP and 14 mL, with teflon lined caps

D. Chemicals

Acetonitrile, HPLC grade
nitrogen
phosphoric acid
t-butyl ammonium hydroxide

Standard Analytical Reference Material for each analyte.

4. Standards

A. Calibration Standards

Prepare individual stock solutions:
5 mg/mL 2,6-DNT
50 mg/mL NG

Stock Solution A:
Combine 200 µL 2,6-DNT stock and 250 µL NG stock and dilute to 10 mL CH_3CN. Concentration is 0.1 mg/mL 2,6-DNT and 1.25 mg/mL NG.

Calibration standards prepared in 10 mL volumetric flasks adding 50% H_2O/50% CH_3CN.

Cal Std.	µL Stock A added	2,6-DNT	NG
1	10	0.1 µg/mL	1.2 µg/mL
2	20	0.2 µg/mL	2.5 µg/mL
3	40	0.4 µg/mL	5.0 µg/mL
4	80	0.8 µg/mL	10.0 µg/mL
5	200	2.0 µg/mL	25.0 µg/mL

B. Control Spikes

Spike Solutions prepared following chart below:

Spike Solution	Amount Stock	Dilute with CH_3CN to	Concentration
1	1 mL of 5 mg/mL 2,6-DNT	5 mL	1 mg/mL 2,6-DNT
2	0.5 mL of 5 mg/mL 2,6-DNT	5 mL	0.5 mg/mL 2,6-DNT
3	0.5 mL of 5 mg/mL 2,6-DNT 0.625 mL of 50 mg/mL NG	5 mL	0.5 mg/mL 2,6-DNT 6.25 mg/ml NG
4	0.250 mL of 5 mg/mL 2,6-DNT 0.312 mL of 50 mg/mL NG	5 mL	0.25 mg/mL 2,6-DNT 3.12 mg/mL NG
5	0.200 mL of 5 mg/mL 2,6-DNT 0.250 mL of 50 mg/mL NG	5 mL	0.20 mg/mL 2,6-DNT 2.50 mg/mL NG
6	0.200 mL of 5 mg/mL 2,6-DNT 0.250 mL of 50 mg/mL NG	10 mL	0.10 mg/ml 2,6-DNT 1.25 mg/mL NG
7	0.100 mL of 5 mg/mL 2,6-DNT 0.125 mL of 50 mg/mL NG	10 mL	0.05 mg/ml 2,6-DNT 0.62 mg/mL NG
8	0.025 mL of 5 mg/mL 2,6-DNT 0.031 mL of 50 mg/mL NG	5 mL	0.025 mg/mL 2,6-DNT 0.31 mg/mL NG

400 µL of spike solutions 8, 7, 6, 4, 2 spiked onto 10 cm^2 concrete and metal surfaces

200 µL of spike solutions 7, 6, 5, 3, 1 spiked onto 10 cm^2 brick and transite surfaces

Concentration on surface after spiking:
NG - 125 µg, 250 µg, 500 µg, 1250 µg

2,6-DNT - 10 µg, 20 µg, 40 µg, 100 µg, 200 µg.

5. Procedure

Extraction A

1. Spike 10 cm^2 surface sample with acetonitrile spike solution (volume dependent on surface type). Allow solvent to evaporate.

2. Transfer sample to 8 ounce jar and add 20 mL CH_3CN. Cover jar with teflon lined cap.

3. Sonicate for 10 minutes.

4. Transfer extract A to 50 mL volumetric flask, add 25 mL H_2O and bring to volume with CH_3CN.

   Save surface sample for Extraction B.

Extraction B

1. Add 20 mL CH_3CN to jar with surface sample. Sonicate for 10 minutes.

2. Transfer surface sample to a second jar. Add 20 mL CH_3CN and sonicate for 10 minutes more.

3. Combine extracts from steps 1 and 2 and evaporate using nitrogen to less than 5 mL.

4. Transfer evaporated extract to 10 mL volumetric flask. Add 5.0 mL H_2O and bring to volume with CH_3CN. Extract B ready for analysis.

6. Calculations

Calculate found concentration for each analyte in each sample extract from daily calibration data.

Multiply found concentration by extract volume to find total µg in extract. Combine total µg in extracts A and B to find total µg on surface.

7. References

Lakings, D.B., Baker, R.J., and Crook, M.V., "Precision and Accuracy Assessment of the High Performance Liquid Chromatographic Analytical Technique for the Determination of Nitrobenzene (NB), 2,6-Dinitrotoluene (2,6-DNT), Nitroglycerin (NG), and Picric Acid (PA), Midwest Research Institute Technical Report No. 2, USATHAMA Contract No. DAAK11-81-C-0007, May, 1981.

QUANTITATIVE METHOD FOR THE DETERMINATION OF PETN ON SURFACES

1. Application

Method used to extract pentaerythrite tetranitrate (PETN) from metal, brick, concrete, transite surfaces.

A. Tested Concentration Range:

PETN 5.0 $\mu g/cm^2$ to 100.0 $\mu g/cm^2$

B. Sensitivity

Instrument response for PETN is given below:

Concentration	Response
0.50 µg/mL	98025 area units

C. Detection Limit

See Table II-1.

D. Interferences

There were no interferences.

E. Analysis Rate

Six samples can be extracted and prepared for analysis in three hours. Rate of analysis is given below, excluding calibration standards:

PETN 32 samples in an 8 hour day

2. Chemistry

Pentaerythrite tetranitrate C5H8N4O12
CAS RN 78-11-5
MP 140-141 C

3. Apparatus

A. Instrumentation

Beckman Model 110A Solvent Metering Pump
Waters Associates Model 450 Variable Wavelength Detector
Waters Associates Model U6K Injector
Hewlett Packard 3390A Integrator/Recorder

B. Parameters

Column: Spherisorb ODS, 5μ, 250 x 4.6 mm ID
Precolumn: Pellicular LC-18, 40μ, 50 x 4.6 mm ID
Solvent System: 65% CH_3CN/35% H_2O
Detector: UV at 230 nm
Flow Rate: 1.0 mL/min
Attenuation: 0.01 AUFS
Injection Volume: 100 μL

C. Hardware/Glassware

Westinghouse Ultrasonic cleaner
8 ounce jars with teflon lined caps
25 mL graduated cylinders
microliter syringes
volumetric flasks - 50, 10, 5 mL
vials - WISP and 14 mL, with teflon lined caps

D. Chemicals

Acetonitrile, HPLC grade
Standard Analytical Reference Material for PETN

4. Standards

A. Calibration Standards:

Prepare stock solution as follows:
200 μL of SARM (50 mg/mL) in 10 mL CH_3CN = 1.0 mg/mL

Calibration Standards prepared in 10 mL volumetric flasks adding 50% H_2O/50% CH_3CN.

Cal. Std	μl Stock added	Concentration PETN
1	5	0.5 μg/mL
2	10	1.0 μg/mL
3	20	2.0 μg/mL
4	40	4.0 μg/mL
5	100	10.0 μg/mL
6	200	20.0 μg/mL

B. Control Spikes

Spike solutions prepared following chart below:

Spike Solution	Amount Stock	Dilute with CH_3CN to	Concentration
1	12.5 µL of 50 mg/mL	5 mL	0.125 mg/mL
2	50 µL of 50 mg/mL	10 mL	0.25 mg/mL
3	100 µL of 50 mg/mL	10 mL	0.50 mg/mL
4	100 µL of 50 mg/mL	5 mL	1.0 mg/mL
5	125 µL of 50 mg/mL	5 mL	1.25 mg/mL
6	500 µL of 50 mg/mL	10 mL	2.5 mg/mL
7	500 µL of 50 mg/mL	5 mL	5.0 mg/mL

400 µL spike solutions 1,2,3,5 and 6 spiked onto 10 cm^2 metal surfaces

200 µL spike solutions 2,3,4,6,7 spiked onto 10 cm^2 concrete, transite, and brick surfaces.

Concentration of analytes on surface after spiking: 50 µg, 100 µg, 200 µg, 500 µg, 1000 µg.

5. Procedure

1. Spike 10 cm^2 surface sample with acetonitrile spike solution (volume dependent on surface type). Allow solvent to evaporate.
2. Transfer sample to 8 ounce jar.
3. Add 12 mL CH_3CN. Cover jar with teflon lined cap. Sonicate for 10 min.
4. Transfer extract to 50 mL volumetric flask.
5. Repeat steps 3 and 4 twice, adding extracts to same 50 mL volumetric flask.
6. Rinse jar with 17 mL H_2O and transfer to volumetric flask.
7. Bring to volume with CH_3CN.
8. Ready for HPLC analysis.

6. Calculations

Calculate found concentration for each analyte in each sample extract from daily calibration data.

Multiply found concentration by extract volume to find total µg in extract.

7. References

None

TABLE IV-4. RESULTS OF ANALYSES FOR RDX, TNB, TNT, AND TETRYL IN CONDUCTIVE NON-SPARKING FLOORING SAMPLES

	Total Micrograms			
Sample	RDX	TNB	TNT	Tetryl
Roll Flooring	48	ND	23	5.4
Roll Flooring (duplicate)	34	ND	7.3	3.2
Travelled Flooring	1200	3.6	890	ND
Travelled Flooring (duplicate)	750	15	2600	ND

ND = Not Detected

heterogeneously throughout the wood. Changes in the sample preparation procedures or analytical conditions which would circumvent this problem were not identified. In any case, further developmental effort should be based on knowledge of what wood type (i.e., species) and conditions (age, moisture content, etc.) best represent actual field conditions.

V. CONCLUSIONS AND RECOMMENDATIONS

- Review of the available literature suggests that available methods for the sampling and analysis of explosives/explosive residues have been developed principally for the identification of post-blast residue and for the detection of concealed bulk explosives. Most of the work in these areas has been directed toward the application of classical spot test methods, thin-layer chromatographic methods, and vapor phase detection methods. None of these methods satisfies all of the Army's requirements for the sampling and analysis of explosives/explosive residues on building materials surfaces.

- A method for the detection of explosives/explosive residues on building materials surfaces based on the formulation of charge-transfer complexes between the explosives and anthracene applied to the surface with visual identification has been developed and evaluated in the field. This method offers the following advantages:

  (1) Sensitivity down to concentrations of analyte(s) on the order of micrograms per square centimeter of surface;

  (2) Speed;

  (3) Manageable hazard during and subsequent to use as compared to similar spot test methods; and

  (4) Reversibility: the charge-transfer complexes formed in this application can be destroyed relatively easily leaving the original analyte intact and available for subsequent quantitative testing.

  Field evaluations performed at two Army Ammunition Plants confirm that this method is, in fact, capable of detecting explosives contamination under field conditions, and that the presence of dirt and debris of the type under such conditions apparently does not result in false positive findings.

- Methods for the determination of explosives/explosive residues on building materials surfaces based on solvent extraction using ultrasonic agitation and analysis by high pressure liquid chromatography have been developed and evaluated in the laboratory. For the majority of analyte-surface combinations studied, analyte recoveries of 60-95% and detection limits on the order of micrograms per square centimeter of surface were obtained.

- The theoretical and practical feasibility of a method for the detection of explosives/explosive residues on building materials surfaces based on UV irradiation with subsequent detection has been demonstrated. This approach may provide the means for "scanning" of an area on a real-time basis to determine whether explosives are present. Further development of this approach is recommended.

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